

***94-1 Research and Development Project
Lead Laboratory Support***

Status Report

July 1— September 30, 1997

Los Alamos
National Laboratory

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*Compiled by
Nora Rink*

Los Alamos

National Laboratory
Los Alamos, NM 87545

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**Compiled by
Nora Rink**

ABSTRACT

This status report is published for Los Alamos National Laboratory 94-1 Development (R&D) projects. The Department of Energy Office of Environmental Management (DOE/EM) funds these projects to support the storage or disposal of legacy plutonium and plutonium-bearing materials resulting from weapons production throughout the DOE complex.

This report summarizes status and technical progress for Los Alamos 94-1 R&D projects during the fourth quarter of fiscal year 1997.

INTRODUCTION

This is the eighth status report published for Los Alamos 94-1 Research and Development Project. The project is funded by DOE-EM to provide support for storage or disposal of legacy plutonium and plutonium-bearing materials resulting from weapons production throughout the DOE complex.

Descriptions and milestones for FY 1997 Los Alamos 94-1 Research and Development projects are found in report LA-13261-SR, "94-1 Research and Development Project Lead Laboratory Support Technical Program Plan."

Figure 1 presents the work breakdown structure for this effort.

Most of the 94-1 R&D project work is conducted at Los Alamos. Three projects, *Nitric Acid-Phosphoric Acid Oxidation*, *Immobilization of Rocky Flats Graphite Fines Residues*, and *Plutonium Phosphate Solution Chemistry*, are conducted at Savannah River Site. *Pyrochemical Salt Filtration* is done at Lawrence Livermore National Laboratory. Pacific Northwest National Laboratory contributes to *Vitrification Issues with Rocky Flats Environmental Technology Site Ash and Sand, Slag, and Crucible* and to *Mediated Electrochemical Oxidation*.

The projects *Catalytic Chemical Oxidation* and *Plutonium Diffusion Science* have been terminated.

The *Mineral Waste Forms* project has been combined with *Thermodynamics* and is reported under that heading this quarter. The projects *Actinide-Organic Interactions* and *Nondestructive Assay-Gamma Salts* are not reported this quarter.

Most activities in the CMR building, which houses the bulk of Chemical Science and Technology (CST) Division operations, were taken out of service the first week of September to assure proper work control. Operations will be restarted using a resumption approach plan. The projected date for full operation is January 1998. Many 94-1 R&D projects are feeling the effects of this temporary cessation of activities.

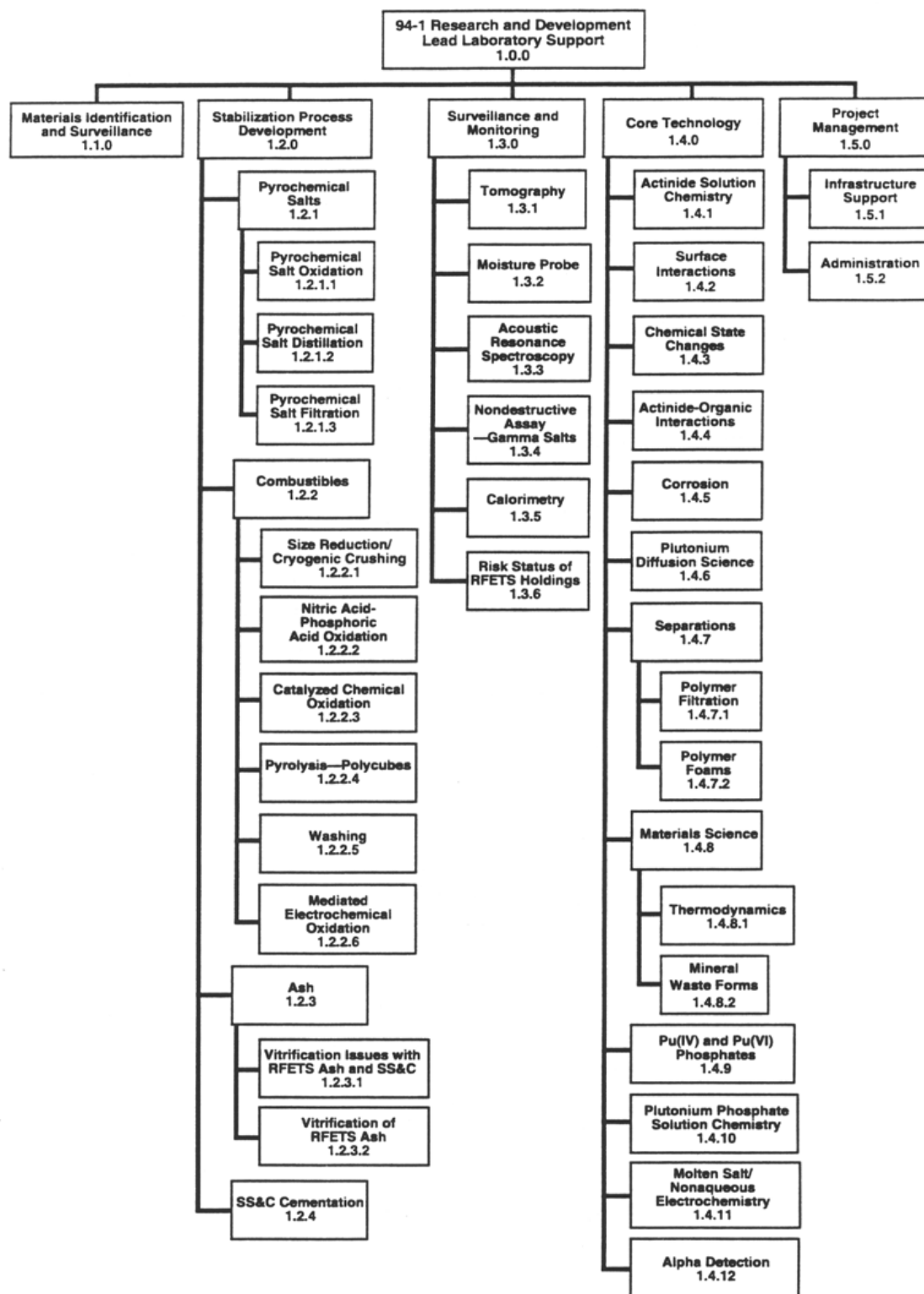


Fig. 1. Work breakdown structure.

Materials Identification and Surveillance

Principal Investigators: David R. Horrell and Richard E. Mason

Task Description. The Material Identification and Surveillance (MIS) project identifies materials to be stored in DOE-STD-3013 containers and determines the processing necessary for the stabilization of these materials. The MIS working group that oversees this work is composed of individuals from Rocky Flats Environmental Technology Site (RFETS), Babcock and Wilcox Hanford Company (BWHC), Savannah River site (SRS), and Los Alamos. Representative plutonium oxide materials destined for 3013 storage are shipped to Los Alamos where we will characterize them and determine their storage behavior. Also at Los Alamos, we are developing methods to increase the accuracy and efficiency of characterizing a variety of materials, modeling thermal profiles of materials in storage configuration, conducting experimentation on thermal profiles to support the modeling, and conducting lid deflection tests on RFETS British Nuclear Fuels, Limited (BNFL) containers using radiography.

Status/Accomplishments

Shipments. A shipment of 10 RFETS items was received in August, completing the transfer of 24 items to Los Alamos for evaluation in the MIS project.

Item Evaluations. Item evaluations are on hold pending resumption of CMR building operations. Calcination and characterization for particle size/surface area, density, and water uptake are complete on three Rocky Flats items as-received and calcined at 950°C; however, we will not begin evaluation of additional items until samples can again be sent to the CMR building for analysis. Analytical capabilities at the CMR building were taken out of service in the first week of September 1997. Operations there are expected to resume in January 1998.

Verification of Calcination Furnace Temperatures. The accuracy of temperature measurement during calcination runs is being verified using temperature indicator pellets made by Tempil, Air Liquide America Corporation. The pellets have a guaranteed accuracy of $\pm 1\%$ of their rated temperature. By procedure, the temperature of the calcination oven is measured using two thermocouples with independent readouts, one to control the furnace and the second to control the over-temperature controller and a temperature recorder. These two readouts normally agree within a few degrees over the entire temperature range from ambient to 1000°C. To verify temperature measurements for the MIS project, three Tempil pellets that melt at 927°C, 954°C, and 982°C are placed in stainless

steel cups on top on the material to be calcined. At a 950°C furnace setting, the 927°C melted but the 954°C pellet did not. With a setting of 960°C, the 927°C and the 954°C pellets melt and the 982° pellet does not melt. The pellets are used with each 950°C calcination run. The 600°C temperature will be similarly verified.

Loss-on-Ignition Evaluation. A review titled "Evaluation of the Loss-on-Ignition Measurement for Storage of Legacy Plutonium-Bearing Materials"¹ evaluates and compares the procedures for the loss-on-ignition analysis followed by Los Alamos, RFETS, and SRS. In this article, we point out that experimental results have shown that the processing times required to bring the materials into conformance with DOE-STD-3013 vary greatly depending on the identity and concentration of the impurities. We suggest that the suitability of LOI analysis in certifying impure plutonium oxide materials for storage is questionable.

Some interesting points on the general usage of LOI became noticeable by reviewing the LOI measurement as practiced within the DOE complex:

- Sites are emphasizing different phases of the procedure in regard to precision for the LOI measurement.
- Sites are using differing amounts of plutonium dioxide sample. This affects the precision of compared results.
- Sites are using differing LOI conditions (time and temperature), and in general, differing LOI temperature profiles.
- Sites are using crucibles for the LOI measurement that are not always made of the same material. Sometimes this is observed even within the same DOE site.
- The suitability of LOI analysis in certifying impure plutonium oxides for storage is fallacious, and additional work is needed. This additional work should focus on determining of how much of the weight loss on ignition is due to volatile materials other than water and whether there is an off-setting component of weight gain.
- Only by being rigorously consistent with time and temperature during calcination and LOI measurement will it be possible to make decisions with confidence for storage involving impure oxides.
- Initial results indicate that supercritical fluid extraction is a possible analytical method for the determination of water content in inorganic matrices, but the method needs to be further developed in order to include hydrogenous organic substances and relatively strong-bonded water of hydration or fixed OH groups.

- Supercritical fluid extraction could be used as a supplementary method to the LOI method.

Thermal Modeling and Temperature Measurements for British Nuclear Fuels Limited (BNFL) Containers. The inner and outer BNFL consolidated procurement cans for the metal storage temperature measurement experiment were welded successfully. Experiments with helium and other gases will begin soon.

Thermal Analyses of Containers and Experiments. As a follow-on to our earlier work determining the thermal response² of plutonium metal and PuO₂ in BNFL containers systems in support of RFETS and its interim storage facility, we have benchmarked the analysis methodology used in the earlier study to a computational fluid-dynamics (CFD) code CFX-F3D and begun the analyses of the container experiments. Our original study used a nodal-network methodology (or thermal-resistance formulation) to describe the temperature field and the heat-transfer processes in and around the container system. This methodology has the advantage of being flexible and relatively easy to apply to complex geometries, but it does not represent fluid convection (actual movement of gas from one node to the next) very well. The CFX-F3D code is more difficult to apply to container geometry but represents a large improvement in the treatment of convection heat transfer.

With the support of the Nuclear Materials Storage Facility Renovation Project, we analyzed one case from our earlier study with the CFX-F3D code and compared the results from the two analyses. The selected case was for two plutonium buttons in a container system surrounded by air. The CFX results agreed reasonably well with the earlier results, and we attributed the lower maximum plutonium temperature (3.6°F or 2°C lower) primarily to the geometry-modeling constraints in CFX that resulted in better thermal coupling between the plutonium buttons and the bottom of the Vollrath convenience jar.

The MIS Project has funded the analyses of its container experiments. These experiments utilize a short, right-circular cylinder ingot of plutonium, and the current data are for argon gas both inside and outside the containers. Because of the reduced thermal conductivity of argon relative to the helium that we assumed to be the fill gas in the earlier analyses, radiation heat transfer increases in importance relative to convection. We have set up the input model for these experiments and performed the initial analyses, which show the maximum plutonium surface temperature to be higher than measured. We are in the process of resolving problems with CFX regarding the way in which the thermal conductivity is averaged between cells, and expect subsequent calculations to reduce the difference between the calculations and the experiment.

Alpha-Beta Phase Transformation Experiment. After 25 transformation cycles between alpha-beta and beta-alpha phases, the density of this alpha ingot changed from 19.37 g/cm³ as cast to 17.21 g/cm³. The density change is calculated at 0.089 g/cm³ per cycle. The experiment is described more fully in our previous quarterly report.³ We analyzed and calculated the density change for the plutonium rod pictured in the Plutonium Handbook,⁴ and the density change appears to be approximately 0.097 g/cm³ per cycle. The strain data clearly show that the maximum stress on the storage container was measured during the first expansion. The strain has steadily decreased to its minimum strain after eight cycles. The data indicate that the container stress has reached a plateau and is not affected by the increasing microcracking and consequent volume change of the plutonium ingot.

Another experiment with an alpha rod (4.49 in. long x 0.4193 in. diam) is completed. We cut this rod to fit across the can as shown in Fig. 2. The rod was positioned lengthwise with a 0.002-in. gap between the rod and inner diameter of the can. Only two expansion cycles were completed using this rod because it bent approximately 0.125-in upward and produced very little stress on the container during the second cycle. The first expansion cycle of the rod against the container wall showed a strain of 2700 micro-strain, which is one third of the strain measured by the first expansion of the ingot.

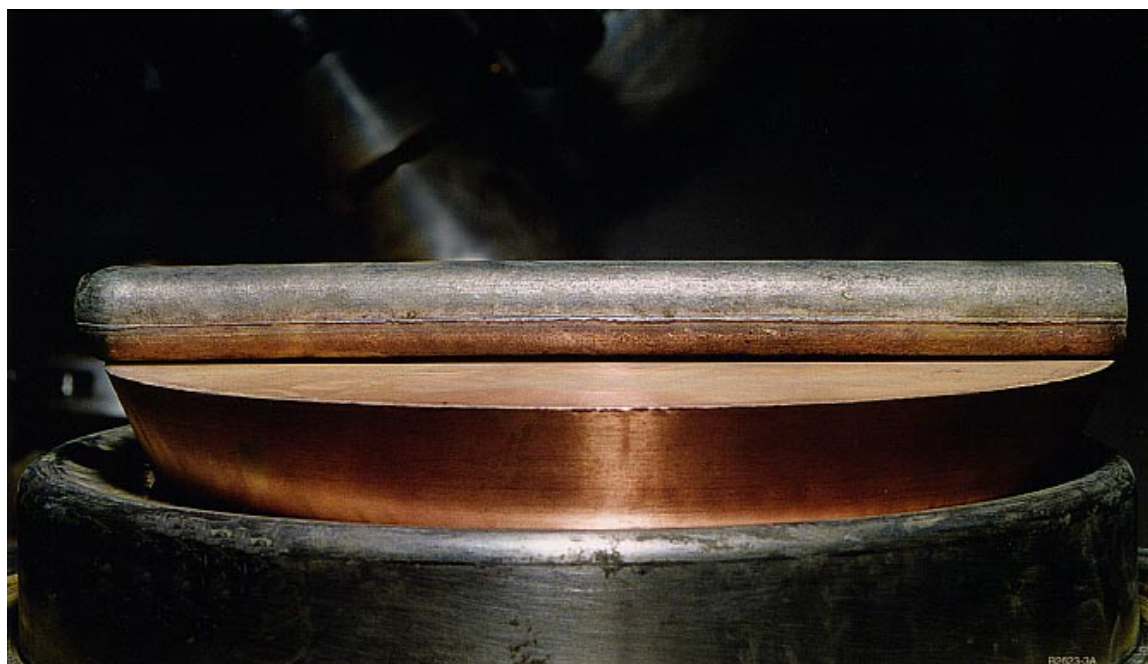


Fig. 2. Alpha plutonium rod used for phase transformation experimentation.

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1. Andreas Toupadakis, "Evaluation of the Loss-on-Ignition Measurement for Storage of Legacy Plutonium-Bearing Materials," Los Alamos National Laboratory report LA-UR-97-3753 (September 1997).
2. Thad D. Knight and Robert G. Steinke, "Thermal Analyses of Plutonium Materials in British Nuclear Fuels, Ltd., Containers," Los Alamos National Laboratory report LA-UR-97-1866, June 1997.
3. Nora A. Rink, Comp., 94-1 Research and Development Lead Laboratory Support, Status Report, April 1-June 30, 1997, Los Alamos National Laboratory report LA-UR-97-3177 (September 1997).
4. "Plutonium Handbook-A Guide to the Technology," O. J. Wick, ed., (The American Nuclear Society, La Grange Park, Illinois, 1980) p. 111.

***Stabilization Process Development:
Pyrochemical Salts—Pyrochemical Salt Oxidation***

Principal Investigator: James McNeese

Task Description. Our task is to demonstrate treatment methods for oxidizing reactive or wet pyrochemical salts. The objective is to develop and transfer to Rocky Flats Environmental Technology Site (RFETS) technology that will stabilize reactive metals in pyrochemical salts and minimize corrosion from water interactions with the salts and with their containers or drums. We are optimizing the oxidation process that prepares feed for salt distillation to be installed at RFETS. We are also determining the effectiveness of liquation of the pyrochemical salts after oxidation to establish the feasibility of a settling technique as a method of decreasing the amount of salt feed requiring distillation.

Status/Accomplishments. In stabilization of sodium chloride/potassium chloride pyrochemical salts, we can distill the oxidized salt to separate plutonium-lean salt that meets safeguard termination limits (STL) from a plutonium-rich distillation heel. To engineer a distillation unit for RFETS implementation, it is required to change the chemical oxidant. The previously chosen oxidant, sodium carbonate, causes foaming in the distillation process and is therefore not suitable for the distillation of molten salt extraction (MSE), electrorefining (ER), and salt scrub (SS) salts. Vanadium pentoxide (V_2O_5) was chosen as the oxidant for further consideration. The fourth quarter was spent developing the oxidation parameters for ER and MSE salts using the V_2O_5 . We have determined that the oxidant in combination with oxygen sparging will give a satisfactory performance in oxidation and salt distillation for these salts.

Current work is based on minimizing the amount of oxidant in both ER and MSE salts in order to meet the 0.2% STL and to meet the DOE standard DOE-STD-3013 criterion of >50 wt% plutonium concentration in the plutonium heel. Efforts are underway to get representative RFETS salts shipped to Los Alamos for demonstration testing to assure that the process parameters will be satisfactory for the mixture of salts held at the site.

Sodium carbonate should remain the oxidant of choice for the stabilization of DOR and other calcium chloride-containing salt residues. The use of vanadium pentoxide to stabilize the calcium chloride salts is feasible but has not been confirmed.

***Stabilization Process Development:
Pyrochemical Salts: Salt Distillation***

Principal Investigator: Eduardo Garcia

Task Description. In this project, we demonstrate equipment designed to carry out the salt distillation process. The salt distillation process is designed to separate plutonium pyrochemical salts into a very lean fraction (<0.2 wt% plutonium) and plutonium oxide suitable for storage under DOE Standard 3013. The chloride content of the pyrochemical residues are converted into totally stable, slightly contaminated salt, and the plutonium content is separated into a homogeneous, well characterized oxide material suitable for long-term storage. An alternate process that uses an aqueous dissolution and filtration separation will be investigated for calcium chloride salts.

Status/Accomplishments. During the fiscal year, we made 85 runs with the full-scale prototype unit in a plutonium glovebox. This includes a total of 29 runs during the present quarter. These feed salts included 15 electrorefining residues and 11 molten salt extraction residues. The only oxidant, with one exception, was vanadium pentoxide (V_2O_5), or a combination of V_2O_5 and oxygen. The sole exception involved a salt oxidized with sodium carbonate and allowed to remain molten for two days before removing it from the furnace.

The large number of feed salts oxidized with vanadium pentoxide have now led to some systematic observations. Electrorefining (ER) salts were processed satisfactorily for the most part. Only two of the distilled salts did not meet the safeguards termination limit (0.2 wt. %), and these were only slightly above the criterion (0.34 and 0.32 wt %). The plutonium percentage of the ER distillation heels ranged from 46-61 wt%. Processing of molten salt extraction (MSE) salts, on the other hand, was generally unsatisfactory. The distilled MSE salts for which a reliable plutonium assay is available contained a very high plutonium concentration. The concentrations for five salts ranged from 0.45 to 1.9 wt%. The blue color of these salts leads to the conclusion that plutonium is present as plutonium chloride and that some chemistry must be occurring in MSE salts that is not present in electrorefining residues. The most likely cause of this chemistry is the large amount of magnesium chloride that was added to these salts when the MSE process was carried out at Los Alamos. The current thought is that the magnesium chloride is reacting with the added vanadium oxide so that some plutonium remains unoxidized. This in turn has led to ever increasing amounts of added vanadium oxide to compensate for the effect. Unfortunately, this exacerbates the problem of low plutonium content in the distillation heels. The plutonium content of the heels ranged from 16-41 wt%. There is a correlation with the plutonium content in the distilled salts: the runs with low plutonium concentration in the distilled salts also had a low plutonium

concentration in the heels. In other words, runs in which a large amount of vanadium oxide was used as the oxidant reduced the amount of plutonium in the distilled salt, but of course led to low plutonium concentration in the heel.

Unfortunately, it is difficult to say how best to overcome this problem, since in the interest of time, the oxidation reactions have not been characterized and the actual chemistry is unknown. One possible solution would be to simply oxygen-sparge the MSE salts, since they contain very little if any plutonium metal. Plutonium trichloride will be oxidized by oxygen, while magnesium chloride will remain unaffected and should be distilled along with the alkali metal chloride salt. This should result in an almost pure plutonium oxide heel. The presence of plutonium metal in ER salts renders them unsuitable for oxygen-sparge treatment.

***Stabilization Process Development:
Pyrochemical Salts—Salt Filtration***

Principal Investigator: Bartley B. Ebbinghaus, Lawrence Livermore National Laboratory

Task Description. The task is to test molten salt filtration as a means to separate and stabilize actinides from spent pyrochemical salts. The process uses a porous ceramic crucible (e.g. zirconia or alumina between 70 and 82% dense) as the filtration medium and is easily adaptable to existing processing equipment and equipment planned for the Rocky Flats Environmental Technology Site (RFETS). To perform these tests, we at Lawrence Livermore National Laboratory (LLNL) are using standard pyrochemical furnaces in argon atmosphere gloveboxes. For initial work, we are using our own limited supply of spent salts, primarily CaCl_2 electrorefining salts that are approximately two to five years old. These salts are similar in composition to direct oxide reduction (DOR) salts in that they are composed primarily of CaCl_2 . Unlike DOR salts, however, the LLNL salt residues generally contain 10 to 20 wt% actinide; some PuCl_3 , which is soluble in molten CaCl_2 ; and in some cases significant quantities of MgO crucible pieces. For more recent work, actual DOR salt residues with about 0.2 wt% actinide have been prepared.

Status/Accomplishments. Experimental work this quarter was brought essentially to a stand-still due to a recent procedural infraction that put the LLNL plutonium facility in a standby status. Although the facility is anticipated to return to operational status sometime in October, no further work is planned on the molten salt filtration task. A brief summary report is in preparation and will be available in the near future. A short summary of the work and conclusions follow.

Both porous zirconia and alumina crucibles were tested. There was no obvious advantage for either filtration crucible type.

Salts with various actinide contents were tested with porous zirconia crucibles. Salts with higher contents of actinide and other insolubles such as MgO crucible fragments filtered significantly slower.

Both calcium-rich and pyro-oxidized salts were tested. Calcium-rich salts cannot be filtered. If the salts contain any residual calcium dissolved in the salt, they must be pyro-oxidized before filtration.

Alumina crucibles with average pore sizes of 3 μm , 40 μm , and 100 μm were tested. Of the three, the 40- μm pore size is most appropriate for the filtration process. Nominal filtration conditions are 4 hours at 900°C.

In conclusion, molten salt filtration is a relatively slow but viable process for separating and stabilizing actinides from spent pyrochemical salts. Actinide separation efficiencies are high and the filtered salt is always well below the safeguard termination limit of 0.2 wt% residual actinide. Additional processing is required to remove residual salt from the pores of the filtration crucible and from the residue concentrate. It was shown that this separation can be performed in a subsequent aqueous filtration step, but the process is very slow.

***Stabilization Process Development:
Combustibles—Size Reduction/Cryogenic Crushing***

Principal Investigator: Horacio E. Martinez

Task Description. In this project we demonstrate size reduction technologies for combustibles. Cryogrinding is a process of size reducing materials at low temperature.

Status/Accomplishments. The HEPA filter remediation system, in which a potential dangerous layer of nitrated wood is removed from the outer surface of the wooden filters by an automated shaving process, is ready to be shipped and installed at the Rocky Flats Environmental Technology Site (RFETS).

In July 1997, the HEPA filter jointer was reviewed by the wet-combustibles group from RFETS. Don Dustin, Rick Ames, John Ryan, and John Dirkes traveled to Los Alamos to review the progress. In September 1997, Rick Ames visited and performed a design review also. As a result of these two reviews, additions and tests have been made.

Los Alamos provided Rocky Flats with chips from different depths of cuts for the nitrate depth test. Each depth of cut was then analyzed at Rocky Flats to determine how much wood to be removed from the HEPA filters. Chips were also provided to Rocky Flats to determine the ignition temperature of the wood. The results of the analysis are summarized in a memo from Richard Ames to Don Dustin dated September 22, 1997.¹

Some of the hardware changes to the jointer are follows:

- A larger chip collector with easier sack attachment was built to use the larger RFETS nylon sack.
- A special felt filter bag and housing were made for the outlet of the vacuum blower motor.
- A lower rpm motor is used to slow down the jointer blades so that if they hit a nail there will be less degradation of the blades.
- Safety shields were made to cover the wheels on the carriage.
- A nitrogen purge has been added to the filter carriage.
- Lifting hooks have been added to the jointer base and angle iron frame.

- Bare metal surfaces have been epoxy-painted.
- Support frames have been built that will attach the jointer base and motor to the top of the shredder already in the RFETS glovebox.
- A locking device on the motor mount has been added to prevent the belt from loosening.
- A split belt guard to facilitate easy cutter head assembly removal has been fabricated.
- New blade guards with captured screws have been made to fit near the pillow blocks.
- O-ring seals have been added to the idler pulley carriage wheels to keep the grease clean in the wheel bearings.
- An easy-to-clean hopper that attaches the vacuum hose to the bottom of the jointer housing has been fabricated.
- The electronics have been mounted in a NEMA enclosure with an emergency stop button.
- A remote control box with an emergency stop button has been made.
- An interlock switch has been added to the carriage lid.
- The gas control solenoids have been mounted in a NEMA enclosure with a flow regulator.

The HEPA filter system will be reviewed again in early October by RFETS personal. Operators will observe our operation and receive initial training on the system. The system will be delivered to Rocky Flats, and we will provide assistance for the installation and operation of the system. It is estimated that this initial installation will require a moderate amount of time. After installation, we will continue to provide support to Rocky Flats as they operate and test the system.

Reference

1. Memo NMT-2:FY97-261, from Richard Ames, Los Alamos National Laboratory group NMT-2, to Don Dustin, Safe Sites of Colorado, "Differential Thermal Analysis (DTA) of HEPA Filter Frame Dust," September 22, 1997.

***Stabilization Process Development:
Combustibles—Nitric-Phosphoric Acid Oxidation***

Principal Investigator: Robert A. Pierce, Savannah River Site

Task Description. Savannah River Technology Center is developing a system for treating radioactive-contaminated organic materials. This program will test and verify the applicability of the nitric-phosphoric acid oxidation system for combustible organic compounds contaminated with plutonium. Other associated tasks will develop a sensor for in-situ monitoring of key compounds in the oxidation process, measure plutonium fractionation during operations, measure potential off-gas emissions, and verify the final immobilization of the resulting acid-metal mixture. Our radioactive demonstration of the nitric-phosphoric acid process will complement nonradioactive pilot testing to be conducted in a Mixed Waste Focus Area Program. Together, the two programs will essentially complete development of this system to treat Rocky Flats combustible residues, SRS Pu-238 contaminated organics, and other commercial nuclear wastes.

Accomplishments/Status. The following is a brief update in each of the areas of testing being conducted with radioactive and nonradioactive materials.

Plutonium Testing. Acid solutions used during the processing of radioactive-contaminated organics were successfully converted into both iron phosphate glass and magnesium-potassium phosphate ceramic final waste forms. The acid contained the metals byproducts of paper, rubber, and plastic compounds along with trace plutonium and 3 g/L uranium. Glass samples were made by using three compositions:

- (1) 30% Fe_2O_3 , 5% Na_2O , 2.5% SrO , and 62.5% P_2O_5 ;
- (2) 20% Fe_2O_3 , 4% Na_2O , 2.0% SrO , and 74% P_2O_5 ; and
- (3) 40% Fe_2O_3 , 6% Na_2O , 3.0% SrO , and 51% P_2O_5 .

Samples 1 and 3 made good glass samples, consistent with earlier experiments. The glass samples await the availability of resources for leach testing.

The solutions were also formulated into two ceramic compositions based on discussions with Dileep Singh of Argonne National Laboratory. The first sample used 30 g 90% H_3PO_4 , 29.7g H_2O , 19.5 g KOH , 13.8 g MgO , and 10.6 g of KH_2PO_4 . We started with the H_3PO_4 and then gradually added a mixture of the KOH and water over a 20- to 25-min period. Next, a mixture of the MgO

and KH_2PO_4 was added all at once. The solution was stirred for seven minutes and then poured into a mold. The solution was stirred in the mold for an extra two minutes before being allowed to cure over the next 30 to 45 minutes. The sample was allowed to cure for two weeks before being submitted for leach testing.

In the second sample, the water content was reduced by 4.2 g. Once again, we started with the H_3PO_4 and then gradually added a mixture of the KOH and water over a 20- to 25-min period. Then a mixture of the MgO and KH_2PO_4 was added all at once. Because of the reduced water content, the second sample got much hotter and began to set up quicker. The sample was stirred for 1 min (as compared to 7 min in sample 1) before being poured into the mold. The sample was stirred an additional 3 to 4 min before it began solidify to an extent that stirring was stopped. The sample was allowed to cure for two weeks before submitting for leach testing.

The samples were leach tested using a modified toxicity characteristic leaching procedure (TCLP) method. The results show that silicon, PO_4^{3-} and NO_3^- leach from the second sample at 2 to 3 times the rates observed in the first sample. Furthermore, the first sample showed less than 0.007 mg/L magnesium leached versus 309 mg/L magnesium for the second sample. Discussions with Dileep Singh indicated that the differences are linked with the rapid solidification of the second sample in that it did not have sufficient time to cure properly. Due to problems in the analysis, samples had to be re-submitted for analysis of potassium and uranium; magnesium leach rates will also be confirmed at that time.

Spectrophotometer Development. During the past quarter, techniques were developed for at-line monitoring of nitrate in the hot, concentrated phosphoric acid matrix. The analyzer consists of a short pathlength (0.025-mm) stainless glow cell with fused silica optics, uv grade fiber-optic cables, a xenon flash lamp for high uv output, and a HP-8452 spectrophotometer. A three vector Principle Components Regression (PCR) model is used to measure nitrate concentration over a range of 0.1 to 1.2 M in the concentrated phosphoric acid. Early tests determined that a dilution of the sample in water at proportions up to 1:50 helped eliminate interference produced by incomplete reaction of organic matter and contributions from metals dissolved in the mixed acid process.

After testing multiple pump and static mixer combinations, we have identified a set-up capable of delivering low sample volumes with sufficient precision to provide accurate at-line measurements. The 4-channel peristaltic pump selected has 8 rollers and is adjustable in 1% increments over its speed range. This approach also eliminates variations caused by using two independent pumps. Both glass and nylon static mixers were tested to assure

sufficient mixing between water and sample, and it was found that the nylon did not have sufficient chemical resistance.

Testing first focused on a 1:4 dilution and it was shown that nitrate concentrations could be accurately measured as the concentration varied between 0.2 and 1.5 M. A known volume of phosphoric acid was heated and batch additions of nitric acid were made; the response was then measured and judged consistent with the amount added. Successful operation was then verified during the addition of organics to the mixed acid bath. Nitric acid depletion was monitored and found to be consistent with prior batch-scale testing.

A minor setback occurred when soluble iron was added to the system. At the 1:4 dilution, it was observed that part of the iron spectra overlapped the measured region for nitrate. To compensate for this, the measure nitrate region was narrowed and the dilution was increased to 1:10. When this was done, the spectrophotometer once again provided an accurate, at-line measurement of nitrate concentration. Experiments using prepared standards mixed in with actual process measurements yielded an observed accuracy on the order of ± 0.04 M nitrate (2 sigma). Although the current requested accuracy is 0.05 M, it is believed that higher levels of accuracy can be obtained if needed.

Offgas Testing. On the bench scale, in a system containing 200 mL of phosphoric acid, a series of tests that covered the range of temperature, pressure, and nitric acid composition were conducted and off-gas and charcoal filter residue samples were collected and evaluated. Next, a series of tests with dioxin precursors was performed. The dioxin-precursor test procedure for the bench scale batch is as follows:

- (1) Pentachlorophenol (PCP) is added to the phosphoric acid batch to serve as a benzene ring (necessary for a dioxin precursor) with available chlorine at room temperature.
- (2) About 0.2 g cupric chloride is added to the concentrated phosphoric acid, also at room temperature.
- (3) The batch is heated to 130°C; then nitric acid equivalent to 2 M batch solution is added.
- (4) The batch is heated to 150°C; then 0.5 g cellulose (paper) waste is added.
- (5) The temperature of the batch is ramped from 150°C to 185°C over an hour period.

- (6) After 15 minutes at 185°C, the process is shutdown. The flask of water used for the first scrub and a charcoal filter in-line at the off-gas exit point to the hood are submitted for dioxin analysis.

The water wash was found to contain a total of 0.2 ppm mixed ketones. Ketones are generally thought of as neutral, mobile volatile liquids that are the second step in the oxidation of a hydrocarbon. No chlorinated or aromatic compounds were found. No residue was found in the activated carbon filter downstream of the water and peroxide washes.

The residual concentrated phosphoric acid batch liquid was analyzed following the completed series of eight wet oxidations of paper, neoprene, and other waste types. The residual batch solution contained both chlorinated pyridine and nitrochlorobenzene, but no other related compounds. The amount of chlorinated pyridine was determined to be about 5 ppm and nitrochlorobenzene, 0.037 ppm. There were no phenols or dioxins identified in solution.

A wrap-up bench scale test subsequent to the series of pilot and bench tests was conducted with a mixture of trichlorophenol (TCP) and PCP as dioxin precursors. The test evaluated a mixture of 3.5 g paper, 1 g polyethylene (PE), 1 g neoprene, 1 mL HCl, and 10 mg each of TCP and PCP. Temperature and pressure were at 185°C and 8 to 10 psig. A number of analytes was detected in the water sample but not in the charcoal filter. There were no phenols or other dioxins present above to the limit of detection. Alkyl nitrates were present in the water sample at 7.7 mg/mL of sample water concentration, as well as 440 µg/mL of short straight chain chlorinated hydrocarbons, such as dichloropentane and dichloropentanol; these are likely products from neoprene destruction. The limit of detection for all analytes, including dioxins, phenols, aromatics, alkyl nitrates, and other alkyl substituted organics in the water sample was 2.0 µg/mL. No analytes were detected in the charcoal tube, at a limit of detection of 10 µg/tube.

Subsequent tests were conducted in the 40-L pilot system. Two tests were conducted with batch samples of 22 g cellulose, 5.2 g PE, 3.5 g neoprene, and 3.5 g polyvinylchloride (PVC) in 16.5 L of phosphoric acid. The waste batch was added at 155°C for one test and 170°C for the second. A third test was conducted with 30 g cellulose, 15 g neoprene, 4.5 g PE, and 5 mg each of TCP and PCP. The phenol mixture was added at 155°C and later ramped to 170°C. First water wash and charcoal filter in the off-gas were analyzed after the second test and after the third test.

The water wash for both tests had an organic mix of 2 to 4 ppm alkyl nitrates and 0.02 to 0.10 ppm parachloronitrobenzene. It is postulated that chlorobenzene was released from the batch at about 130°C and reacted with nitrous oxides in the gas phase before condensing in the water wash. Also,

because the benzene compound was present both from the test with and without phenols but not from small-scale tests not using PVC, it is believed that it is an impurity used in PVC manufacturing. Throughout pilot testing there were no dioxins or phenols detected.

Issues. Availability of resources resulted in not being able to complete leach testing of radioactive glass samples. These have been made and are awaiting analysis. Also, because of problems observed in the leach testing of magnesium-potassium phosphate ceramic samples, the samples need to be resubmitted for analysis of potassium and uranium leach rates.

***Stabilization Process Development:
Combustibles—Pyrolysis of Polycubes***

Principal Investigator: Daniel J. Kathios

Task Description. Various sites in the complex manufactured cubes formed of plutonium and uranium oxides cast in a polystyrene matrix for criticality studies. Approximately 1600 cubes in storage at Hanford now represent a waste that is not suitable for long-term storage. The aim of this project is to design, test, and deliver to Hanford a pyrolysis system that will effectively destroy and remove the polystyrene matrix, leaving the oxides as free-flowing powders that are suitable for either dissolution or long-term storage. Pyrolysis is a pyrochemical technique whereby a high temperature inert environment is used to break down and volatilize polymeric materials. Following pyrolysis, an off-gas treatment oxidizes the organic constituents. Secondary combustion, catalytic conversion, and silent discharge plasma (SDP) are being considered for the treatment of the pyrolysis off-gas. Based on an engineering study, Hanford selected SDP as the preferred option. Work will proceed towards logical hold points for all off-gas technologies until the technical maturity of the SDP can be demonstrated for this application.

Status/Accomplishments

Off-Gas Technologies

Secondary Combustion. The hold point for this off-gas treatment technology was reached during the second quarter of FY97 with the completion of the design and procurement specifications.

Silent Discharge Plasma (SDP). All work on the development of the SDP was discontinued at the end of July because of cost overruns for the task. After the program office and SDP's parent organization addressed the overrun issues, only one activity critical to resolving a shipper-receiver difference was allowed to resume work. We will resume SDP activities in FY 1998.

Catalytic Conversion. We completed assembly of the catalytic conversion system last quarter and began demonstrating the full-scale system in June. The full-scale system includes a pyrolysis reactor, condensate collection reservoir, condensate pump, revaporization chamber, and catalytic reactor. A second, essentially identical system is being assembled for implementation at Los Alamos.

Pyrolysis System Testing. We processed a total of 26 polycubes during the fourth quarter. The composition of the catalytic conversion process off-gas

demonstrated almost complete conversion to carbon dioxide with only small quantities of carbon monoxide detected. A short burst of noncondensable, gas-phase hydrocarbons was observed during the initial polycube decomposition. The oxidation efficiency for these gas-phase hydrocarbons was greater than 90% and a corresponding burst of hydrocarbons was observed in the system off-gas. The oxidation efficiency for the liquid-phase hydrocarbons ranged from 99.998% with a condensate feed rate of 0.1 g/min down to 99.989% at 0.7 g/min. The combined gas- and liquid-phase oxidation efficiency was greater than the required 99%.

The cycle time for the process was determined to be 10 h per cube, with 70% of the cycle time required for cooling the reactor before recharging. Slightly less than 3 years would be needed to process the 1600 polycubes at Hanford with the full-scale catalytic conversion process.

During a previous test, a graphite-like carbon deposit caused the line to plug at the point where the condensate combined with the preheated air upstream of the catalytic reactor. A vertical revaporization chamber was added to remove the entrained particulate material. After 10 cubes were processed, the revaporization chamber was replaced and the chamber containing the deposit was placed in the pyrolysis reactor for processing. When the revaporization chamber was removed from the pyrolysis reactor only a graphite skeleton remained. We estimate that 10-15% of the deposit was re-pyrolyzed.

It is not known whether the particulate is formed as the polycubes decompose in the pyrolysis reactor or when the reactor off-gas is condensed. The same material was observed when the SDP unit was disassembled in June during the Hanford project review. Since the SDP unit had been operated with both condensate and direct pyrolysis off-gas, further testing will be needed to determine the source of the particulate material. We also observed that the generation rate of the carbon particulate was noticeably reduced when post-pyrolysis residues were removed from the reactor. The potential for particulate carryover from the pyrolysis reactor will be investigated during FY98 to support the development of the SDP system.

***Stabilization Process Development:
Combustibles—Washing***

Principal Investigators: Norman C. Schroeder and Moses Attrep, Jr.

Task Description

Nitrate-Contaminated Combustibles. The first objective of this task is to test a proposed Rocky Flats Environmental Technology Site (RFETS) process flowsheet designed to stabilize nitrate-contaminated wet combustible residues by washing them first in dilute caustic, then twice in water, and then drying them. The experimental plan consists of work with small- (1-g) and large- (100-g) scale wet combustible surrogate material. Non-radioactive experiments are performed with ^{141}Ce -traced ceric ammonium nitrate ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$) and ^{141}Ce -traced cerium oxide (CeO_2). Radioactive experiments are performed with trace levels and macro quantities (5.8 mg) of plutonium nitrate ($[\text{Pu}(\text{NO}_3)_6]^{-2}$) and plutonium oxide (PuO_2). The second objective of the task is to evaluate alternative drying strategies that could be used in lieu of absorbents. Based on a list of criteria, we will select two alternative drying candidates.

Organic-Contaminated combustible residue treatment. The objective of this task is to test a proposed RFETS process flowsheet designed to remove organics (cutting oils) and solvents (carbon tetrachloride) from combustible residues and to stabilize finely divided plutonium metal contaminants in these residues.

Status/Accomplishments

Nitrate-Contaminated (Wet) Combustibles. We are investigating alternative drying processes for stabilized wet combustibles and working to define the optimum parameters for the selected process. We conducted a series of experiments to select the most promising drying procedures. The selection has taken place. This report deals with the hot-forced-air-procedure parameter optimization and concludes this study.

Bagged wet surrogates (1 kg) were used to determine the parameters for drying in a forced air drying chamber. Two preparations were analyzed:

- (1) a 50% plastic and 50% paper preparation and
- (2) a 90% plastic and 10% paper preparation.

The experiments were conducted in a stainless steel chamber using heated air. The surrogate was thoroughly soaked in water and pressed dry. The weighed bag was then placed in the chamber and covered. Measurements of the weight of the wet bag were usually taken at 0, 30, 60, 90, and 120 minutes. Thirty-seven experiments were conducted and the following observations are given:

- The drying rate of the wet surrogate increases with increasing temperature and with increasing flow rate, and it is enhanced when the heating chamber is heated.
- It is possible to lose as much as 6 g/min water under the conditions of ~125 L/min air flow, in-going temperature equals 120°C, and the heating chamber heated not greater than 120°C.
- The integrity of the plastic bags was not breached after repeated rewetting and rigorous squeezing for removing the excess water.
- The 90% plastic-10% paper surrogate retained less water than the 50%-50% surrogate when pressed. The 90% plastic-10% paper surrogate dried faster than the 50%-50% surrogate under the same conditions.

We conclude that forced-heated-air drying is a viable means for drying the wet surrogates. Operational issues of multiple chambers being performed simultaneously and management of the high volume of gas in the negative pressure glovebox must be addressed.

No future work is planned; the project is completed. A report by Moses Attrep, Jr., and Leonard R. Quintana titled "Forced Air Drying Experiments for Two Surrogates," has been issued LA-UR-94-3887).

Organic-Contaminated Combustible Residue Treatment. We tested a proposed process designed to stabilize organic-contaminated combustible materials that contain plutonium metal. The three original steps in the process were to

- (1) wash cutting oils from the combustibles with a solvent, carbon tetrachloride (CCl_4)
- (2) perform a low temperature thermal desorption (LTTD) of the solvent from the combustibles, and
- (3) stabilize the plutonium metal by low temperature steam oxidation.

The inert atmosphere glovebox containing a 2-gal Parr reactor located in the Alpha Facility [glovebox] at TA-48 has successfully passed all safety evaluations. Initial experiments with a new batch of Rocky Flats combustible surrogate material were problematic. Cooling the reactor was significantly more difficult

than when the reactor was not enclosed. Heat transfer to the surrogate was significantly decreased [over experiments in the open room], possibly because we used the larger cut of the new surrogate. Packing 500 g of the new surrogate into the reactor basket container required that it be compressed to fit into the basket. The old surrogate did not require any compression. These problems caused over-heating and melting of the outer surrogate material, but slower desorption of the CCl_4 during the LTTD. Straight CCl_4 (100 mL) can be distilled from the reactor, through a HEPA filter, to a trap outside the glove box, in 30 minutes. Only 35 mL of CCl_4 could be desorbed from the new surrogate in this time period. The heat transfer problem for the LTTD could possibly be alleviated by using a hot nitrogen flow. This capability is being designed into the Rocky Flats process for water removal and could be applied to the LTTD. The lower heat transfer to the surrogate requires 20% more hot water to be injected into the reactor for the steam oxidation; thus 600 mL of water per 500 g of surrogate was required to maintain an active steam environment; i.e., enough free water is left after the surrogate becomes saturated to transfer heat from the reactor wall to the surrogate.

Small scale (~0.1 g) steam oxidation experiments with alloyed plutonium metal turnings were conducted in the glovebox with 300-mL and 2-gal Parr reactors. Experiments were conducted with cutting-oil-coated and clean, hexane washed, turnings. Oxidations were carried out at 110°C for 2 h at approximately one atmosphere above ambient pressure; steam concentrations ranged from 50 to 100%. Metal samples were exposed directly to the steam or submerged in water. No reaction occurred when either oil-coated or clean metal was submerged. This is contrary to previous cerium metal results, which showed that 4 g of cerium turnings, oil-coated or clean, could be oxidized under these conditions when submerged. Oil-coated plutonium was nonreactive when exposed to steam, while 30-50% oxidation occurred for the clean metal. The degree of oxidation was determined by a visual decrease in the metal size and observed gas generation when treated with 1 M sulfamic acid. Breaking the metal turnings (specific surface area $<10 \text{ cm}^2/\text{g}$) into smaller pieces had no effect on the extent of oxidation. Calculations show that surface area is only increased by ~20% by breaking the turning into 100 pieces; the specific surface area is still $<10 \text{ cm}^2/\text{g}$. The water oxidation rate of the metal observed in these experiments is slower than expected for unalloyed plutonium but significantly faster than that expected for alloyed plutonium. The turnings may have microscopic cracks that significantly increase the surface area relative to their geometric surface area, and that may account for oxidation rate observed. However, the oxidation rate still needs to be accelerated to fit into the time allowed for the oxidation step in the proposed stabilization procedure. Lastly, submerging the turnings in water appears to passivate the metal turnings. All oil-coated turning that were submerged in water during the reaction were less reactive to sulfamic acid than the starting oil-coated metal.

Process experiments must to be conducted to determine the maximum amount of time needed for carbon tetrachloride desorption and complete oxidation of the metal by steam oxidation.

***Stabilization Process Development:
Combustibles: Mediated Electrochemical Oxidation***

Principal Investigator: Wayne Smith (Los Alamos) and Dean Kurath (Pacific Northwest National Laboratory)

Task Description. The mediated electrochemical oxidation (MEO) project is being carried out at two sites, Pacific Northwest National Laboratory (PNNL) and Los Alamos National Laboratory, with both efforts aimed at the destruction of combustible residues. The project is a back-up to the current baseline treatment technology and is under continuing development to address specific RFETS needs. The project consists of three components:

- (1) development at PNNL of a process flow sheet for the treatment of Ful-Flo™ filters,
- (2) re-engineering of the current PNNL CEPOD II unit to accommodate the Ful-Flo filters, and
- (3) continuing studies at Los Alamos of the MEO process parameters with the goal of optimizing the treatment process.

Status/Accomplishments.

Modified MEO Flow Sheet. The first task was completed in December, 1996. PNNL personnel provided a modified MEO flow sheet for the treatment of Ful-Flo filters. This flowsheet estimated the liquid volume generated in the treatment process using either ion exchange or oxalate precipitation to recover the plutonium. Also taken into account was whether or not the nitric acid solution would be recycled or sent to liquid waste treatment. An initial estimate of liquid waste generated in treating the filters by MEO was approximately 115,000 liters. The modified Ful-Flo filter flow sheet estimated the liquid waste volumes at approximately 13,000 to 38,000 liters depending on the which plutonium recovery/acid recycle path was chosen. Even the worst case combination, which generates the 38,000 liter liquid waste stream, is considerably less than the original process estimate. The results of this study are summarized in the FY 1997 second quarter 94-1 R&D report¹.

Pre-Conceptual Design Description. The second task was completed in August, 1997. PNNL personnel provided a pre-conceptual design description based on a modified CEPOD II dissolver which was previously fabricated for use at the Plutonium Finishing Plant at the Hanford site. This work is contained in a formal PNNL internal report².

The pre-conceptual design incorporates the addition of anolyte and catholyte recycle loops to convert the batch electrochemical reactor to a flow through reactor. This modification allows the filters to be treated in a separate filter housing in the anolyte recirculation loop. Another modification to the electrochemical cell involves decreasing the anolyte volume by increasing the cathode size. This modification allows a higher aqueous concentration of plutonium to be achieved and reduces the volume of aqueous waste that must be treated. Both cerium and silver were considered for use as the catalyst. Cerium is preferred over silver since silver is a RCRA listed metal and its use would lead to the generation of a mixed transuranic waste.

The preconceptual design also includes how the CEPOD II dissolver and the balance of process equipment would be installed in a glovebox. The equipment includes the CEPOD II dissolver, pumps, filter housing, oxalate precipitation tanks, a calciner for converting the oxalate precipitate to an oxide, an off-gas system for reducing NO_x emissions and an evaporator for reducing liquid waste effluents.

MEO Process Parameters. The third task was carried out at LANL and involved a study on the effect of temperature and the choice of redox mediator on the destruction efficiency of organic materials. Styrene-divinyl benzene copolymer based ion exchange resin was the organic material chosen for this study. This material is present as a combustible residue throughout the nuclear complex and it is chemically inert, making it a true test for the MEO waste treatment technology.

Three mediators were investigated, silver(II), cobalt(III) and cerium (IV). The oxidizing power of these mediators in 6 M nitric acid was found to lie in the order: Co(III) > Ag(II) > Ce(IV). All experiments were run at the same current density and with the same concentration of mediator. A summary of the results showing the destruction efficiency of the resin in the presence of these three mediators is given in Fig. 3.

As a baseline, resin was added to the electrochemical cell, the solution was brought up to temperature, and the same quantity of current was passed as in the experiments containing a mediator. At all temperatures investigated the destruction of the resin in the absence of a mediator was negligible, accounting for less than 2 % of the total mass added. These results demonstrate the chemical inertness of the resin even in hot concentrated nitric acid.

At low temperature, 20°C, the resin is destroyed at an efficiency comparable to the oxidizing power of the mediator: Co(III) > Ag(II) > Ce(IV). At this temperature, destruction of the resin with cobalt and silver is slightly greater than 100 % based on the theoretical number of coulombs required per unit weight of resin. The destruction efficiency with cerium as mediator is negligible, essentially the same as with nitric acid alone. At 50°C, all three mediators are

approximately equally effective at destroying the resin. At 70°C, the efficiency with cobalt and silver begin to decline while the efficiency with cerium continues to increase, approaching 400 %. The maximum efficiency obtained with cerium levels off beyond 70°C.

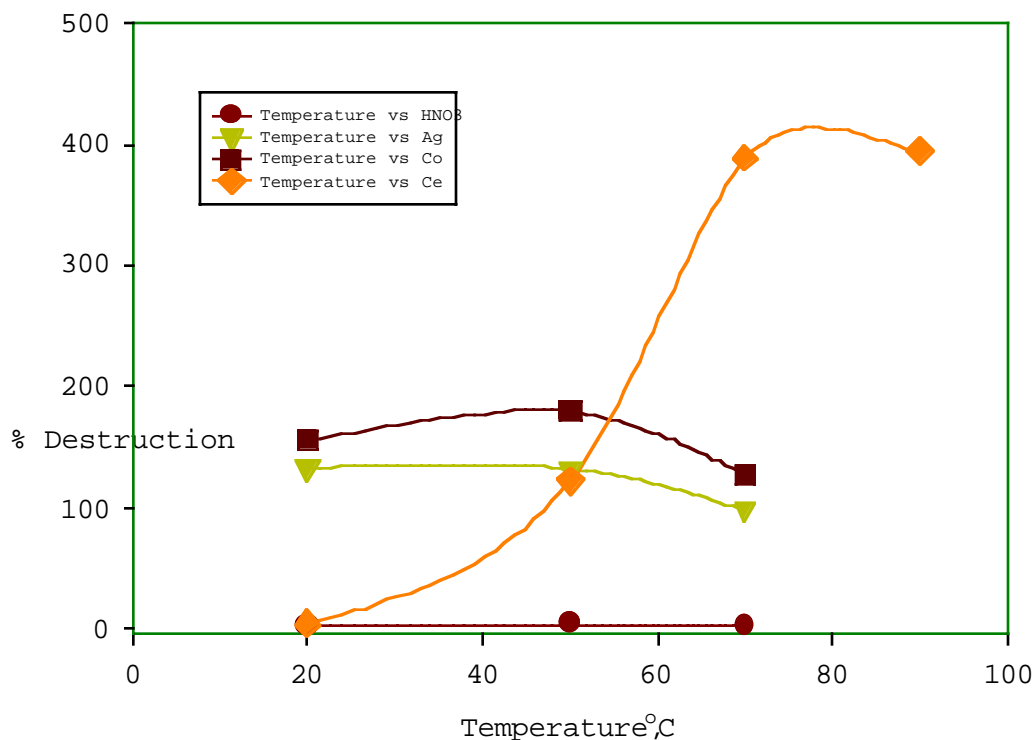


Fig. 3. Destruction efficiency of three mediators in 6 M nitric acid on styrene-divinyl benzene copolymer-based ion exchange resin.

The destruction efficiency of the resin should increase with temperature owing to a corresponding increase in the reaction kinetics. However, there is a deleterious side reaction of the mediator with the solvent, which produces oxygen and reduces the mediator back to its non-reactive lower oxidation state. Apparently the rate of this side reaction increases at a faster rate with temperature than the reaction between the mediator and the ion exchange resin. Thus, the resin destruction reaction appears to slow down at elevated temperatures because of a lower concentration of mediator in solution.

The high destruction efficiencies, approaching 400 %, based on the theoretical quantity of electricity passed, indicate that nitric acid is participating in the oxidation reaction. The baseline experiments in the absence of mediator show the chemical inertness of the resin material. But apparently, when the mediator

attacks the resin and opens the benzene rings, they become more easily oxidizable and susceptible to attack by the solvent.

Under conditions chosen for this study, the optimum destruction efficiencies for ion exchange resins are obtained with the use of cerium as an electron transfer mediator and at a temperature of 70°C. However, 100 % destruction efficiency can be achieved at room temperature using either silver or cobalt as the mediator. It should also be pointed out that each organic compound chosen for treatment by MEO will have its own set of optimized reaction parameters that should be determined prior to treatment of the material.

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Stabilization Process Development:

Ash: Vitrification Issues with Rocky Flats Environmental Technology Site Ash and Sand, Slag, and Crucible

Principal Investigator: Gerald Veazey, Los Alamos National Laboratory and Ja-Kael Luey, Pacific Northwest National Laboratory

Task Description. Our objective in this project is to support Safe Sites of Colorado (SSOC) in developing a vitrified waste form for Rocky Flats Environmental Technology Site (RFETS) ash and sand, slag, and crucible (SS&C). Work on SS&C was put on hold until resolution of whether the SS&C would be sent to Savannah River Site for stabilization. The tasks are to determine nondestructive assay (NDA) constraints and operating parameters for a vitrified waste form and to investigate a conventional furnace system as the technology to produce the vitrified waste form.

Status/Accomplishments

NDA of vitrified waste forms. This task was completed during this quarter with the submittal of the final report by Los Alamos to RFETS in August 1997.¹ The goal of this project was to determine if a segmented gamma scanner (SGS) with 1/2-in. collimation could be used to accurately establish the plutonium content of a glass-based waste form produced with ash similar to that at RFETS. Acceptable accuracy was considered to be within 10 % of the result determined by calorimetry and gamma isotopics. The results of the study showed that the SGS with 1/2-in. collimation can achieve an accuracy of ~6 % using a count time of 20 min. The report also described data collected on the accuracies of an SGS with 2-in. collimation and a thermal neutron counter (TNC). The results of this study should be applicable to other wastes (such as graphite fines) with the same plutonium particle size as long as the final waste form possesses a similar density, geometry, and plutonium homogeneity.

Conventional Furnace Melting. Work continued during this quarter at PNNL on the agglomerated waste form. During this quarter, two frits were identified for further consideration. The selection criteria were that the frits must be able to produce a waste form that will not be susceptible to foaming and will pass the safeguards termination limit (STL) extraction test. The selected frits were a tin-zinc-phosphate (TZP) frit with a processing temperature of as low as 250°C and a high temperature sodium borosilicate (NBS) frit with better performance in the STL extraction test. Subsequent comparison of these frits in STL extraction testing using cerium as a plutonium surrogate showed that, while the TZP frit met the STL standard of 15 g Pu/kg waste form, its performance was a factor of 15 worse than the NBS frit. This finding significantly contributed to TZP being given a

lower priority for future consideration. Several other factors, however, also contributed to this decision. These were

- high-carbon content ashes and waste loadings of ash greater than 20 wt% caused the agglomeration temperature of the TZP frit to increase above 500°C
- increased storage problems of the TZP frit due to its hygroscopic nature, and
- higher cost of TZP frit due to its production method and cost of raw materials.

The concern over foaming with the higher temperature NBS frit prompted a consideration to incorporate into the process prior to agglomeration a calcination step to remove the carbonaceous material responsible for foaming. The removal of carbonaceous material by precalcination would also have the benefit of increasing achievable ash loading in the waste form and eliminating a previously identified problem with inconsistent product quality caused by differing amounts of carbonaceous material in the ashes. Various calcination techniques, such as rotary calcination and pan calcination, are currently being considered. Experimental evaluation of batch calcination was performed at 700°C with four cold ash surrogates sent from RFETS. Weight loss after calcination for Mix A was 6.5 %, and, although some clumping was observed, the clumps had very little strength. Mixes B, C, and D had weight losses of 40.3 %, 26.6 %, and 44.0 %, respectively, with no clumping observed in any sample. These weight losses are the same magnitude as the carbon and organic content in the original material.

Work was also performed with these ash surrogates on characterization of the off-gases generated at temperatures to be encountered during calcination and agglomeration. A literature study was performed to identify the most likely gaseous species to be encountered, focusing on materials considered to be typical components of ash such as paper, polypropylene, and polyvinylchloride. Experimental work was then conducted to collect data on the RFETS surrogates. The data was collected at temperatures of 700°C and during the ramp-up from room temperature to 1000°C. These tests were conducted under an inert atmosphere to simulate the pyrolysis reactions and a 21 % oxygen atmosphere. Analyses were performed by gas chromatography and mass spectrometry. Preliminary results from this study have shown that CO and CO₂ were produced under both inert and oxidizing atmospheres. Under oxygen-deficient environments, however, flammable gases such as methane were also produced. This indicates that an oxidizing atmosphere may be useful in greatly reducing the production of flammable gases. This work will continue in FY 1998 to collect additional data on other ashes and the individual ash components.

Several full-scale tests using calcined and/or low-carbon surrogate ashes were conducted to support the frit development and provide an evaluation of processing techniques under consideration. Work focused on characterizing the

heat transfer to produce an acceptable product. The use of metal fin inserts was investigated as a means of increasing the heat transfer and was found to be effective. Tests were also conducted at calcined ash loadings of 20 wt%, 40 wt%, and 67 wt% to determine the effect of ash loading on heat transfer. The tests were conducted at 800°C with the samples kept in the furnace for 2.5 h. Temperature measurements at the centerline (5 cm from bottom) showed that the 20 wt% and 40 wt% samples reached at least 700°C, indicating that the quality of the final product would be expected to be high. The 67 wt% sample, however, showed much slower heat transfer, reaching a maximum of only 600°C.

Work on the flowsheet development task was completed in September with the submission of a draft report² on September 30, 1997. This report summarizes all flowsheet development activities and provides a recommended process option for RFETS ash. This recommendation contains a pre-calcination step. The inclusion of this step will allow for other processing and product constraints to be met, e.g., processing temperature below 800°C, processing time less than 4 hours, and formation of an agglomerated product that meets STL criteria.

Reference

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***Stabilization Process Development:
Graphite Fines: Immobilization of Rocky Flats Graphite Fines Residues***

Principle Investigator: T. S. Rudisill, Savannah River Site

Task Description. The Savannah River Technology Center (SRTC) is developing an immobilized waste form for graphite fines residues generated during nuclear materials production activities at the Rocky Flats Environmental Technology Site (RFETS). This residue category was generated during the cleaning of graphite casting molds. Its nominal composition is 85 wt % graphite, 10 wt % calcium fluoride (CaF_2), and 5 wt % plutonium oxide (PuO_2). The CaF_2 was used as a coating on the casting molds to minimize the chemical interaction between molten plutonium metal and the graphite mold. Plutonium metal present during the cleaning process was most probably oxidized to PuO_2 ; however, this cannot be confirmed without a detailed examination of the residues and is a potential concern. Approximately 950 kg of graphite fines are currently stored at RFETS.

The preferred disposition technology for graphite fines is immobilization by mixing and heating with a diluent to stabilize the residue and produce a waste form which meets the safeguards termination limit (STL). In its present state, plutonium in graphite fines is considered *difficult* to *very difficult* to recover,¹ which allows termination of physical protection if the plutonium concentration is less than 0.2 wt % or protection measures equivalent to Category IV requirements if the plutonium concentration is less than 1.0 wt %. Since the nominal PuO_2 concentration is 5 wt %, the immobilization process must meet the intent of the safeguards termination criteria by limiting plutonium recoverability. The recoverability of plutonium in the immobilized waste form will be subject to product acceptance criteria currently under development by RFETS. The criteria will specify dissolution conditions and time during which a specified plutonium recovery must not be exceeded.

Status/Accomplishments. A second plutonium recoverability experiment was performed with the immobilized graphite fines waste form to confirm its dissolution behavior under conditions specified by the RFETS product acceptance criteria. Graphite fines were simulated by mixing filings from a graphite rod with 10 wt% calcium fluoride (CaF_2) and 5 wt% plutonium oxide (PuO_2). As in the previous experiment, the waste form was fabricated by diluting 10 g of simulant with 40 g of -40 mesh alkali borosilicate glass frit, mixing, and heating at 750°C for 1 h. See Table 1 for composition. The waste form was crushed with a hammer until all pieces passed through a 3/8-in. sieve. The waste form pieces were then leached in 9 M nitric acid/0.25 M CaF_2 solution under reflux

Table 1. Glass Frits Used for Immobilization of Graphite Fines

Component	Alkali Borosilicate (wt%)	Tin-Zinc-Phosphate (wt%)	Sodium Borosilicate (wt%)
Al ₂ O ₃			5
B ₂ O ₃	15		10
CaO	9		
F		2	
Fe ₂ O ₃	6		
K ₂ O	6		
Li ₂ O			5
Na ₂ O	25		15
P ₂ O ₅		60	
SiO ₂	39		60
SnO		28	
ZnO		10	
ZrO			5

conditions for 20 min as prescribed by the RFETS product acceptance criteria. After cooling, the solution was filtered and a sample analyzed by liquid scintillation counting. Based on the results from this analysis, 80% of the original plutonium in the waste form was present in the filtrate or 7 grams plutonium per kilogram of waste form. This value was the same as measured in the previous experiment and exceeded the 4 grams of plutonium per kilogram of waste form specified by the product acceptance criteria.

The focus of additional experiments with graphite fines was improvement of the waste form durability to meet the product acceptance criteria. The waste forms were fabricated, visually examined, and subjected to a qualitative recoverability test if a mechanically durable waste form was produced. Variations in the temperature, frit-to-residue ratio, and frit composition were investigated using this procedure. Experiments with the alkali borosilicate glass frit investigated the effect of temperature and frit-to-residue ratio. Fabrication of the waste form at 950°C, holding all other variables constant, failed to produce a monolithic waste form. At this temperature, the glass frit melted and sank to the bottom of the crucible, leaving a loose layer of simulated graphite fines on the surface. Increasing the frit-to-residue ratio to 8:1 resulted in a mechanically durable waste form. A recoverability test was performed as prescribed by the product acceptance criteria; however, contact with the nitric acid/CaF₂ solution effectively disintegrated the waste form. Waste forms were fabricated with two additional glass frits. Tin-zinc-phosphate and sodium borosilicate glasses (see Table 1) were fabricated and ground to -40 mesh. A simulated graphite fines waste form was fabricated with the tin-zinc-phosphate frit using the same processing conditions as the alkali borosilicate waste forms. The waste form was very hard but disintegrated during the recoverability test. Waste forms were fabricated at 750°C and 950°C with the sodium borosilicate frit using the baseline processing conditions. Both waste forms were somewhat friable. A recoverability test was

performed with the waste form fabricated at 750°C since it was more durable; however, dissolution eliminated any agglomerated material.

Based on the results of the experiments performed with the simulated graphite fines, a waste form fabricated by mixing and heating with a glass frit will not meet the RFETS product acceptance criteria (and, therefore, the STL). There are three alternatives for the continued development of the waste form:

- development of the immobilization process using the alkali borosilicate glass frit could continue assuming justification for a higher plutonium safeguards termination could be developed with DOE concurrence,
- a new immobilization process which meets STL could be developed, or
- the graphite fines could be calcined to remove the graphite.

If the graphite is removed, the remaining material (a mixture of plutonium oxide and calcium fluoride) could be stored and made available to the DOE Materials Disposition Program. The concentration of plutonium would likely approach or exceed 50 wt% in much of the material, allowing storage under the DOE standard for metals and oxides (DOE-STD-3013). Alternatively, an immobilization process could be developed for the calcine, producing a waste form which passes the recoverability test and meets STL. Durable waste forms have been produced with simulated incinerator ashes at both SRTC and the Pacific Northwest National Laboratory. If the carbon content is low enough, as is the case with some incinerator ashes, or is removed by calcination, a durable waste form is obtainable.

Reference

1. Memo "Additional Attractiveness Level E Criteria for Special Nuclear Material," from Edward J. McCallum, Director, Office of Safeguards and Security, NN-51, to Distribution, July 22, 1996.

***Surveillance and Monitoring:
Tomography***

Principal Investigator: Lynn Foster

Task Description. The objective of this project is to evaluate the feasibility of using computerized tomography (CT) as a noninvasive method for determining the contents and conditions of nuclear materials in storage containers. Using surrogate materials, researchers are evaluating commercially-available x-ray tomography equipment for its ability to examine plutonium and plutonium compounds in sealed metal containers. The capabilities of this approach to identify plutonium corrosion products, such as plutonium hydride and plutonium oxide, are being investigated.

Status/Accomplishments. In FY 1997, tomography phantoms constructed jointly by Los Alamos National Laboratory and Savannah River Site researchers were imaged at three different laboratories using commercially available tomographic equipment. The phantoms were designed to test the various CT systems for image resolution of high-density objects and for density discrimination in low- and high-density regions. Los Alamos, Lawrence Livermore National Lab, and AlliedSignal conducted the evaluations. The participating laboratories used several different types of x-ray computerized tomography systems and a wide range of x-ray interrogation energies.

The image data was evaluated and analyzed at Los Alamos National Laboratory. The tomographic data provided by the different laboratories was used to contrast and compare the capabilities of the various tomography systems. The use of dual energy CT for identification of materials was also evaluated. A reconstructed, horizontal slice through a section of one of the phantoms developed for dual energy analysis is shown in Fig. 4. The image shown was taken on a 450 keV x-ray tomography system at AlliedSignal. This section consists of seven sample vials containing different lead compounds and one empty vial packaged in a stainless steel storage container. The differing densities of the compounds are clearly indicated by the image intensity in the reconstructed image.

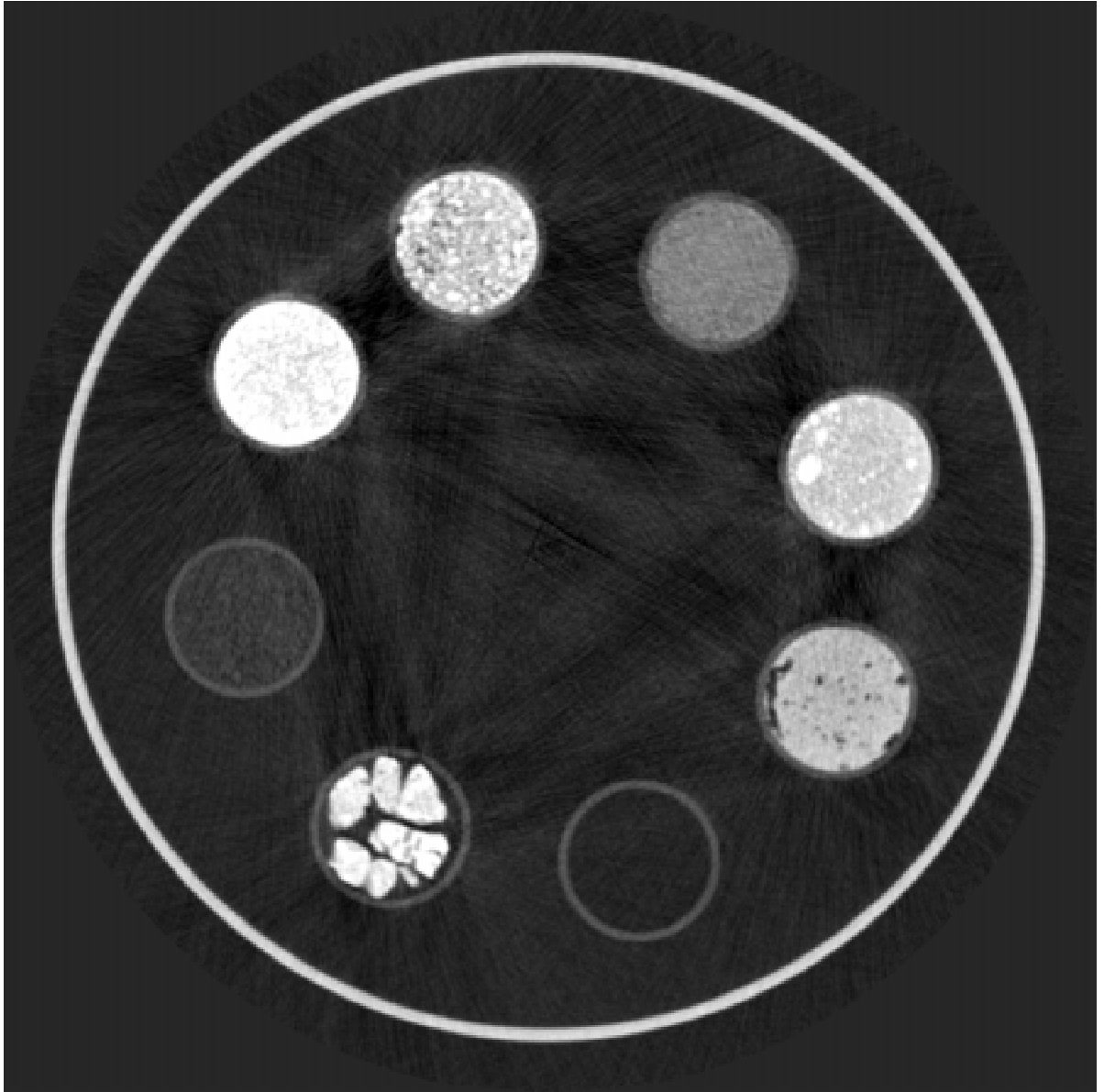


Fig. 4. Horizontal CT image slice through Los Alamos/SRS tomography phantom. High-density/high-Z regions appear as brighter areas in the image.

***Surveillance and Monitoring:
Neutron Moderation for Inspection of PuO₂ Canisters***

Principal Investigator: Lynn Foster

Task Description. A neutron-based moisture probe is being developed jointly by Science Applications International Corporation (SAIC) and Los Alamos National Laboratory.

Status/Accomplishments. Science Applications International Corporation has completed the feasibility study and production of the bench-top model neutron probe for nondestructively verifying the moisture content of plutonium oxide destined for long-term storage. The final report was previously delivered to Los Alamos to satisfy SAIC's commitment for the Phase I feasibility study. Based on theoretical modeling and laboratory measurements on surrogate materials at SAIC, the estimated sensitivity limit of the bench-top model for moisture detection in PuO₂ is 0.06 wt% at one sigma above background. The predicted sensitivity for an optimized engineering prototype system proposed by SAIC is less than 0.02 wt% moisture.

The field test of the bench-top model produced by SAIC has been completed. Los Alamos designed and constructed a special container based on the 3013 storage container. The modified can has six stainless steel tubes penetrating through the center of the plutonium oxide which are welded to the top of the can. The tubes are sealed on the bottom to contain the plutonium oxide and open on the top. This allows the addition of a known, and variable, amount of hydrogen to be placed into the standard by inserting polyethylene rods of varying diameters into the penetrations. The hydrogen content in the polyethylene rods can easily be converted into an equivalent moisture content. This design allows for greater flexibility in varying and quantifying the moisture content, but has a disadvantage in that the moisture is not homogeneously mixed with the plutonium. This disadvantage will be addressed through Monte Carlo modeling of the system.

The modified standard container, designated MISSTD-2, was filled with approximately 2.9 kg of pure plutonium oxide and welded in an inert atmosphere. The plutonium oxide was calcined at 950°C for 2 h before it was packaged to remove any residual moisture from the material. The welded can was removed from the glove box with no detectable contamination on the outer surface. A helium leak check system was used to verify the integrity of the welds.

SAIC shipped the bench-top model and the Cf-252 interrogation source to Los Alamos in August 1997. Measurements were made on the MISSTD-2 standard using the bench-top model. Polyethylene rods of three different diameters were used to simulate varying moisture levels in the plutonium oxide. The response of the instrument as a function of equivalent weight percent moisture content is shown in Fig. 5. The smallest non-zero moisture content shown in the figure is 0.12 wt%. This level is clearly above the detection limit for this instrument. Based on these experiments, the minimum detectable quantity of moisture in this standard is estimated to be 0.04 wt% at one sigma above background. This number agrees very well with the estimated detection limit of 0.06 wt% determined by SAIC during the feasibility study. The experiments show that this system can easily detect quantities of moisture at the 0.5 wt% criteria specified by the DOE-STD-3013 packaging standard.

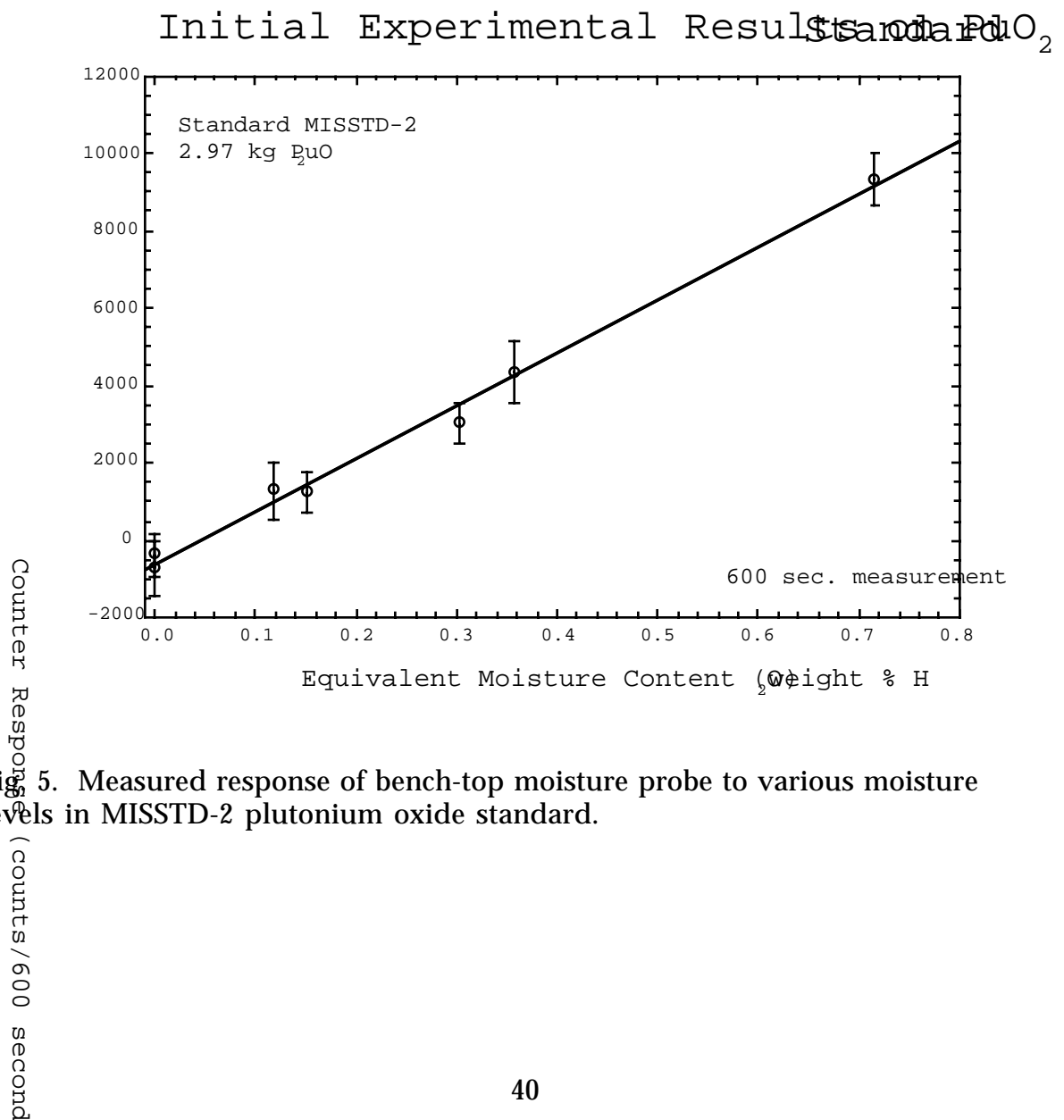


Fig. 5. Measured response of bench-top moisture probe to various moisture levels in MISSTD-2 plutonium oxide standard.

***Surveillance and Monitoring:
Acoustic Resonance Spectroscopy***

Principal Investigators: Kirk Veirs

Task Description. The objective of this project is to develop a noninvasive, nondestructive method for monitoring increases in gas pressure and changes in gas composition within sealed storage containers. The method is based on measuring the properties of standing waves produced in a gas contained within an acoustic cavity using acoustical excitation and detection. The frequency of the standing waves changes with gas composition and the intensity changes with gas pressure.

Status/Accomplishments. During this period, the work accomplished to-date was presented at the National Meeting of the American Chemical Society and was written up for NMT's Actinide Quarterly. Attempts were made to obtain a 3013 Storage Container System in order to test the concept, but so far we have not been successful. The work planned for next quarter is to submit a manuscript on the work to date and continue efforts to obtain a 3013 Storage Container System.

***Surveillance and Monitoring:
Calorimetry***

Principal Investigator: Teresa Cremers

Task Description. In this task, we apply finite element analysis to obtain a model that will predict calorimeter performance and permit the design of smaller, faster calorimeters.

Status/Accomplishments. Researchers from the Engineering Science and Applications (ESA) division Engineering Analysis group completed a low-resolution two-dimensional model of a 6-in. calorimeter. The model will be used to support both the ARIES program and the DOE-STD-3013 needs at Los Alamos and elsewhere, since packages produced by the two programs are similar. This model approximates the ARIES II needs. We are evaluating the predicted performance, and assessing the need to change the design for the ARIES II calorimeter. The ESA efforts also produced 2 minor variations of their model.

The ABAQUS™/Standard finite element analysis tool has been received and installed. The learning curve for this tool is progressing by running some of the vendor-provided exercises. A training seminar will be attended at a later date.

Monitoring and Surveillance:

Risk Status of Residue Holdings at Rocky Flats Environmental Technology Site

Principal Investigator: Tom Rising

Task Description. This task assesses the risk status of Rocky Flats Environmental Technology Site (RFETS) residue holdings described in the Defense Nuclear Facility Safety Board (DNFSB) Recommendation 94-1. At issue is the change in risk status during the past three years resulting from package aging effects and from mitigation efforts such as drum venting and repackaging. The analysis will address the status prior to DNFSB 94-1 remediation efforts, describe the current status, and provide information needed in the development of methodologies for predicting future risk behavior based on various program scenarios. The scope of work for this project was recently changed to include risk analysis of Hanford food-pack cans that are the subject of the Surplus Oxides and Metals Trade Study and work on the Westinghouse Savannah River (WSRC) trade study on the future use of the canyons.

Status/Accomplishments

Surplus Oxides and Metals Trade Study This trade study is almost complete with the selection of alternative 3b, an alternative that features Hanford packaging their material into packages that meet the DOE-STD-3013 standard and sending them to Savannah River as soon as they can. The primary cost driver for this option is the rapid evacuation of Hanford facilities that allows early closure. This early closure provides a savings of \$40 to \$50M per year.

A close second to 3b was alternative 4, which also took advantage of early shipment of materials to SRS, but without first packaging them in 3013 containers. This alternative was somewhat controversial because it called for shipment of material to SRS in the existing food-pack cans. Safety analysis by TSA-7 demonstrated that the food-pack cans could be safely stored and shipped for the required time. WSRC ran an analysis on the thermal effects of the 9975 shipping container that also showed that shipment of food-pack cans is feasible. Therefore, alternative 4 will provide EM with a viable option to alternative 3b. Note that 3b, while being very economical, is more capital intensive than alternative 4, and thus might be favored for cash flow reasons.

The study is essentially complete. Work needs to continue on writing up the final report and the results of the risk analysis.

WSRC Canyon Trade Study Work on the new canyon trade study was initiated with meetings at Savannah River and RFETS. The object of the study is to determine whether or not the SRS canyons should remain in operation beyond the present scheduled shutdown to process materials over and above those presently planned. F Canyon is scheduled to close in 2000, FB line in 2001 and H Canyon in 2004. The study is examining plutonium, HEU, fuels, special isotopes, and holdings at small sites.

Most of the materials that would be candidates for plutonium processing are from RFETS. The large amount of material and the limited processing capability at RFETS makes canyon processing a viable alternative to the baselines. However, several other sites, including Los Alamos have materials that are potential candidates. The Los Alamos materials could probably be most efficiently processed in PF-4, however, there might be other reasons to send them to SRS, especially if Los Alamos is suffering from a vault capacity shortage.

The plutonium team has identified all candidate materials. The next step is formulating representative flow paths so that the various options can be compared and the canyons can be scheduled. The team work should be complete by the end of November 1997, and the overall Trade Study completed by January 1998.

Core Technology:

Actinide Solution Chemistry in Residues and in Residue Stabilization and Treatment Processes

Principal Investigator: John M. Berg and Mary P. Neu

Task Description. In this task, we develop the solution chemistry of actinide elements in legacy residues and proposed residue treatment processes to guide stabilization and disposition decisions and to enable treatment process optimization.

Status and Accomplishments: Effort in the fourth quarter focused on continuing analysis of Pu(IV) nitrate and Pu(IV) chloride speciation information contained in spectrophotometric titration data collected for this project during previous quarters, and on obtaining EXAFS data on the Pu(IV) chloride solution system.

Analyses of Pu(IV) nitrate spectrophotometric data progressed through using Monte Carlo techniques to quantify the confidence levels in the species assignments and equilibrium constants that were derived earlier in FY97 from these data sets. The results confirm that attribution of the observed spectroscopic changes to stepwise addition of the first two nitrate ions is correct to greater than 95% confidence relative to the alternatives of concerted addition of multiple nitrate ions. Uncertainties in the formation constants appear to be on the order of 20% of the measured values. This application of Monte Carlo methods is, we believe, a novel approach to uncertainty analysis in these types of systems. It promises to put these and similar studies on firmer foundation and has the potential to explain inconsistencies in the literature due to poor uncertainty estimates.

Formation constants for Pu(IV) chloride were calculated from our data and appear to be in significant disagreement with literature values derived from ion exchange measurements. Closer examination of our spectroscopic data suggests that an outer sphere complex may be formed at lower chloride concentrations than those needed to form the inner sphere complexes whose formation constants are determined from our analyses. Such an outer sphere complex could bias the results of ion exchange measurements towards higher formation constant values.

EXAFS data on a solution sample of Pu(IV) in 6 M HCl were obtained at SSRL in July. We have begun analyzing those data to determine the approximate average coordination number under those conditions to serve as a reference for the species prepared in the Pu(IV)-Cl spectrophotometric titrations.

The level of effort and rate of spending on this project was significantly reduced during the fourth quarter relative to the first three quarters. This was a planned reduction designed to bring spending in line with allocations at year end. Our level of effort for the first three quarters of the FY exceeded what could be sustained for the full year.

Core Technology:
Chemical and Physical Interactions of Actinides with Surface Substrates

Principal Investigator: David Morris

Project Description. We focus in this project on molecular spectroscopic characterization of the interaction of plutonium and other actinides with important residues including combustibles (ion-exchange resins and cellulosic materials) and incinerator ash.

Status/Accomplishments: Significant new research progress has been made this quarter in the areas of mesoscale imaging and Pu(IV) speciation on aged anion-exchange resins. Details of this work are provided below. In addition, we hosted a one-week consulting visit from Patrick Treado of the University of Pittsburgh to evaluate liquid-crystal tunable-filter (LCTF)-based micro-Raman and Raman imaging instrumentation. Work on evaluation of the nitration hazard for organics in concentrated nitric acid continues, but completion of the report on this subject has slipped to December 1997 as a result of funding limitations. Finally, task personnel were active participants in two international meetings during the quarter and presented four papers on their 94-1 work.

The central goal of our imaging project is to develop techniques for integrating elemental and molecular images from different instruments and evaluating our ability to extract useful information from the data. The main issues involved in the former are spatial registration (making groups of pixels from each image match the same spatial coordinates of the sample) and interpolation (operations to force images from different instruments to a common spatial resolution). The registration problem has been addressed by using a simple 2-point calibration where one point defines the center of the image and a second simultaneously defines both the expansion and the angle relative to the raw Cartesian coordinate system of the image. This approach works when both points can be identified in all images of the set and there are no distortions. The approach is adequate for our needs to date; however, we expect cases to arise where these ideal conditions will not be met, so we continue to pursue more robust methods.

We have shown that resampling of the higher spatial resolution data sets to match the spatial resolution of the lowest resolution image is the most straightforward way to place all images on a common spatial grid needed for further analysis. Other possibilities are interpolation of lower resolution to highest or interpolation of all images to some intermediate resolution. These other approaches increase computation complexity without any obvious benefit and have been set aside.

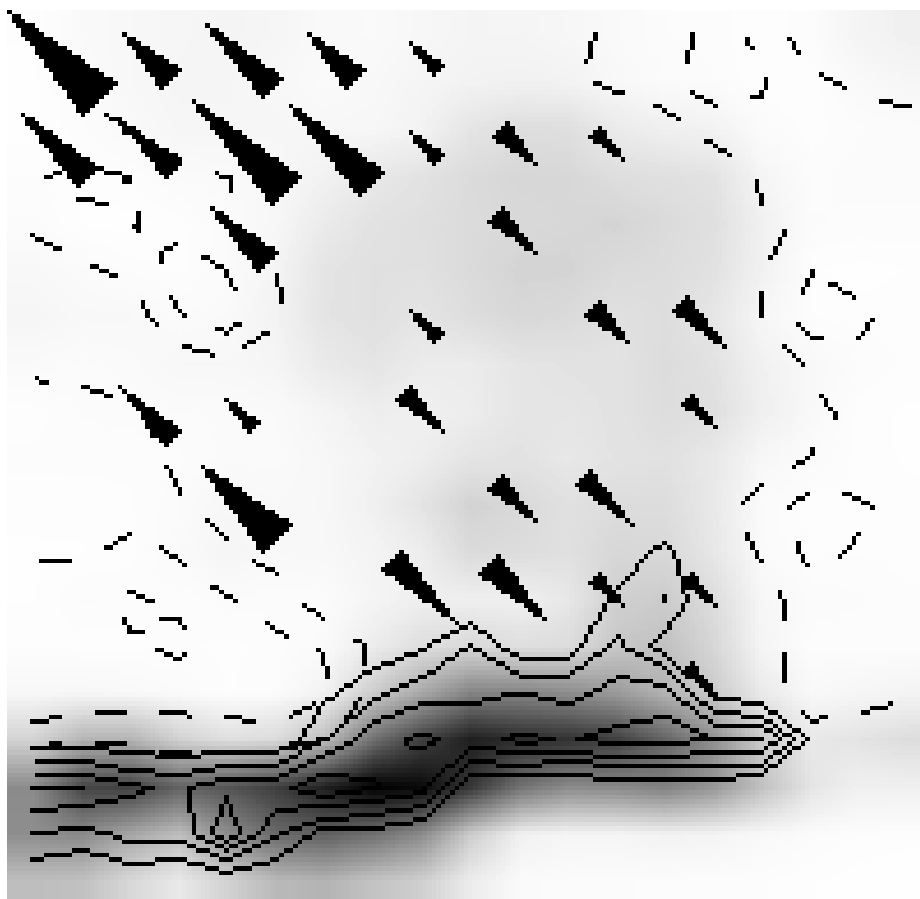


Fig. 6. A combined XRF/ir grayscale image of calcium content of a sample.

A combined x-ray fluorescence/infrared spectroscopy (XRF/ir) image is shown in Fig. 6. The grayscale image is an XRF map of calcium content of a sample. The solid contour overlay indicate regions rich in carbonate which strongly suggests a calcite phase along the bottom of the image. The dashed contours indicate high-silicon regions associated with silica (i.e. quartz) phases. The triangle symbols indicate two types of hydroxyl-bearing phases. Those pointing to the upper left we believe to be mica phases; those pointing to the lower right are iron and calcium-bearing amphiboles. If combined with thermodynamic data, each region may be ranked with respect to its stability, allowing assignment of chemical reaction potential to individual regions within the sample.

During the visit by our consultant, P. Treado, several residue samples were examined in both conventional Raman microprobe and imaging modes using the LCTF technology. The imaging mode seems to provide superior out-of-focus fluorescence rejection, allowing plutonium oxide aggregates to be identified in Rocky Flats ash. Several modifications to our Raman microprobe system are planned based on ideas generated during the consulting visit.

We completed the initial spectroscopic investigations of the speciation of Pu(IV) on Dowex 11 as a function of resin aging during this quarter. As noted previously, because of the high concentration of plutonium in these samples, the spectroscopic data can most easily and efficiently be derived using diffuse reflectance methods. Our initial target in these studies was Pu(IV) in 8 M nitric acid, because this most closely approximates the conditions used in the actual plutonium processing step. Samples were prepared using both fresh resin and resin that has been aging in 8 M nitric acid for approximately 7 months. Samples were prepared at calculated loading levels (assuming the hexanitrate complex of Pu(IV) is the relevant sorbate) of 10% and 100%.

The surface spectral data for these samples indicated that there was little if any change in the Pu(IV) surface speciation as a function of the age of the resin material. This observation is consistent with our previous determination using Raman spectral data that the resin is not appreciably degraded in 8 M acid even after approximately 1 year. We did, however, observe significant measurable changes in the electronic spectral data as a function of the loading level of the resin for both the fresh and the aged resin, and this change is exacerbated for the aged material. The change is manifest in the linewidth of the electronic bands for most of the observed transitions. Linewidth analyses of these data indicate that the Pu(IV) nitrate species at low (10%) loading exist in a homogeneous environment with little interaction between other Pu(IV) species on the resin or with the resin itself. At the higher loading level, the absorption bands are substantially broadened and go from lorentzian to gaussian in character, indicating a new, much greater degree of inhomogeneous interaction. Notably, however, there is not a significant change in the overall spectroscopic signature (band position and intensity) for these samples. The signature is essentially identical to that reported previously by Veirs and Marsh¹ and corresponds to the hexanitrate complex of Pu(IV) on the resin².

References:

1. Marsh, S. F., R. S. Day, and D. K. Veirs. Spectrophotometric Investigation of the Pu(IV) Nitrate Complex Sorbed by Ion Exchange Resins. Los Alamos National Laboratory report LA-12070 (June, 1991).
2. P. G. Allen, D. K. Veirs, S. D. Conradson, C. A. Smith, and S. F. Marsh. Characterization of Aqueous Plutonium(IV) Nitrate Complexes by Extended X-ray Absorption Fine Structure Spectroscopy. *Inorganic Chemistry* **1996**, 35, 2841.

Core Technology:

Identification and Characterization of Changes in the Chemical State of Plutonium in Interim Waste Forms

Principal Investigator: Kirk Veirs

Task Description. This work identifies and characterizes changes in the physicochemical state of plutonium compounds found in residues and stabilized materials. We study plutonium-containing materials other than metal and pure oxide using x-ray absorption spectroscopy (XAS) to identify changes in the local chemical environment of the plutonium metal center. Changes in local chemical environment can indicate the onset of deleterious transformation in the waste form that may lead to unsafe storage conditions.

Status/Accomplishments. During this period the data for two XAS studies were acquired and the work was presented at the Plutonium Futures_The Science Conference, and two international conferences, Actinides '97 Conference, Baden-Baden, Germany and International f-Element Conference, Paris, France.

The June and July experimental run at the Stanford Synchrotron Radiation Laboratory included plutonium carbonate solids. These samples are being used to investigate correlations between oxidation states and x-ray absorption edge energies in the solid phase. A series of plutonium carbonates in various oxidation states has been synthesized. These compounds and their corresponding solution species were characterized using a combination of optical absorbance spectroscopy, diffuse reflectance, and powder x-ray diffraction. The following carbonate solids were prepared, characterized, packaged and shipped to SSRL for XANES measurements: $\text{Pu}_2(\text{CO}_3)_3$, $\text{Na}_6\text{Pu}(\text{CO}_3)_5$, $\text{NaPuO}_2(\text{CO}_3)$, and $\text{Na}_4\text{PuO}_2(\text{CO}_3)_3$. The data will be analyzed in FY 1998.

Analysis of the XAS data for nitrate ion exchange resin samples described in the previous quarterly¹ was completed. The chemical state of the plutonium retained on resin freshly removed from the processing column is significantly different from the chemical state of the aged resin that was characterized in January. The plutonium exists as oxidation states III and IV in the resin freshly removed from the processing columns. The polymeric Pu(IV) hydroxide observed on the aged resin appears to be formed as a result of aging in a wet air atmosphere. Washed resin from the nitrate process retains significant amounts of plutonium in the form of the plutonium hexanitrate complex. Other complexes are present to a lesser extent.

The plutonium species on an anion exchange resin from 8 M HCl is PuCl_6^{2-} . It is observed that the extent of chloride complexation is greater for the plutonium sorbed onto an anion exchange resin than for plutonium in solution. The nitrate

system also exhibits more complete complexation for the plutonium sorbed onto the anion exchange resin as compared to plutonium in solution. This trend is consistent with higher activity coefficients generally observed for species within resins as compared to solutions.

The experimental data obtained this quarter and at the beginning of next quarter will be analyzed and published. The next set of pure reference compounds to be investigated will be plutonium nitrates. Samples with unknown compositions from Rocky Flats and Hanford that are being studied in the shelf life program will be obtained and studied.

1. Nora A. Rink, Comp., 94-1 Research and Development Lead Laboratory Support, Status Report, April 1-June 30, 1997, Los Alamos National Laboratory report LA-UR-97-3177 (September 1997).

***Core Technology:
Corrosion***

Principal Investigator: Darryl P. Butt

Task Description. Our research focuses on the effects of crystallographic orientation on the electrochemical behavior of engineering materials relevant to the Defense Nuclear Facility Safety Board (DNFSB) Recommendation 94-1 by coupling localized corrosion measurements (using a scanning electrode technique) with crystallographic orientation mapping of surfaces (using orientation imaging microscopy (OIM)). On a fundamental level, the goal of this research is to understand the effects of crystal structure on pit initiation and to gain insight into the stochastic nature of pitting. On an applied level, an objective of this work is to recommend processing approaches that promote corrosion resistance of engineering materials.

Status/Accomplishment. Research for the 94-1 core technology corrosion effort was on schedule for the fourth quarter of FY 1997.

Nickel Tests The initial stages of this research were directed towards the production of model materials suitable for study. The study of model materials is a necessary precursor to the study of engineering materials. Research during the previous quarter focused on the microstructure and electrochemical characterization of polycrystalline nickel, single crystal nickel, and stainless steel (SS) materials.

Materials Characterization

Polycrystalline Nickel Material fabricated from powder is required to produce randomly oriented grains. Powder metallurgy (P/M) nickel with randomly oriented surface grains is not commercially available because the processing history of the metal from production invariably results in surfaces having a predominance of one or a few particular orientations. We successfully produced P/M nickel material in the fourth quarter. In contrast to the unacceptable material produced previously, this production run yielded material that attained nearly complete densification. This material is suitable for study. An etch of this material revealed a large grain size which is ideal for study (Fig. 7). OIM of this material is planned for the next quarter. A portion of the P/M nickel was rolled and recrystallized to produce a second texture (not shown). OIM of this material is also planned for the next quarter.



48 mm

Fig. 7 - Micrograph of P/M nickel following etching.

Nickel single crystals We produced (110) and (100) single crystals during the quarter. Upcoming activities include production of more (111) material, as well as (110) material having a different growth direction ((111)) than that produced previously ((210)).

Electrochemical Characterization.

The pitting potentials of different single crystal and polycrystalline materials have been determined (Fig. 8). The pitting potential, the electrochemical potential at which corrosion pits propagate, is a measure of the localized corrosion susceptibility of materials. More positive pitting potentials indicate a greater resistance to pitting. Preliminary tests suggest that the (111) orientation (the close-packed face) is more resistant to pitting than other orientations. We caution that the (111) tests are considered preliminary because there was poor control of the materials preparation prior to these tests. We plan to duplicate the (111) tests. Other tests planned for next quarter will examine the pitting susceptibility of additional polycrystalline textures.

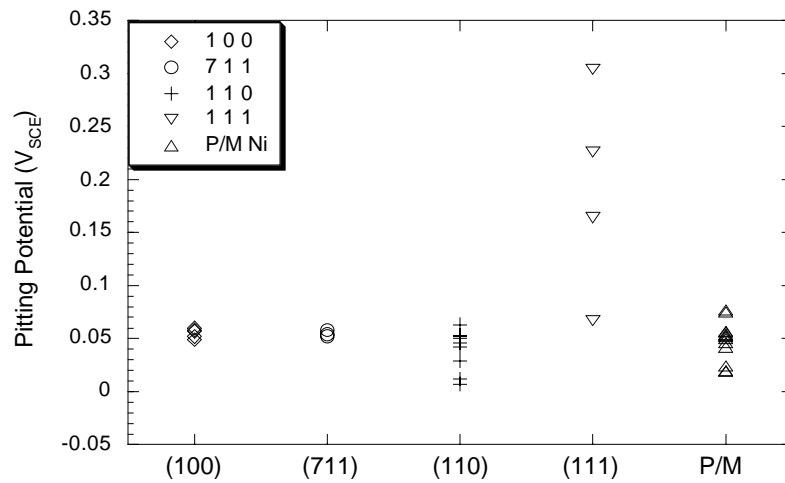


Fig. 8 - Comparison of pitting potentials for different nickel materials.

Stainless Steel Tests Understanding the effects of crystallographic orientation on the corrosion behavior of stainless steel is the ultimate goal of this project. During the past quarter, we attempted to modify the microstructure of 304 SS via heat treatment in order to produce an ideal material for study. The heat treatment was successful in producing a relatively large grain size (on the order of 50 μm) without sensitizing the material. This material was examined via optical microscopy and via OIM (Fig. 9).

Miscellaneous The probes for scanning reference electrode testing (SRET) work are still in production. The patent disclosure for the novel electrochemical cell has been forwarded to the industrial partnership office for review.

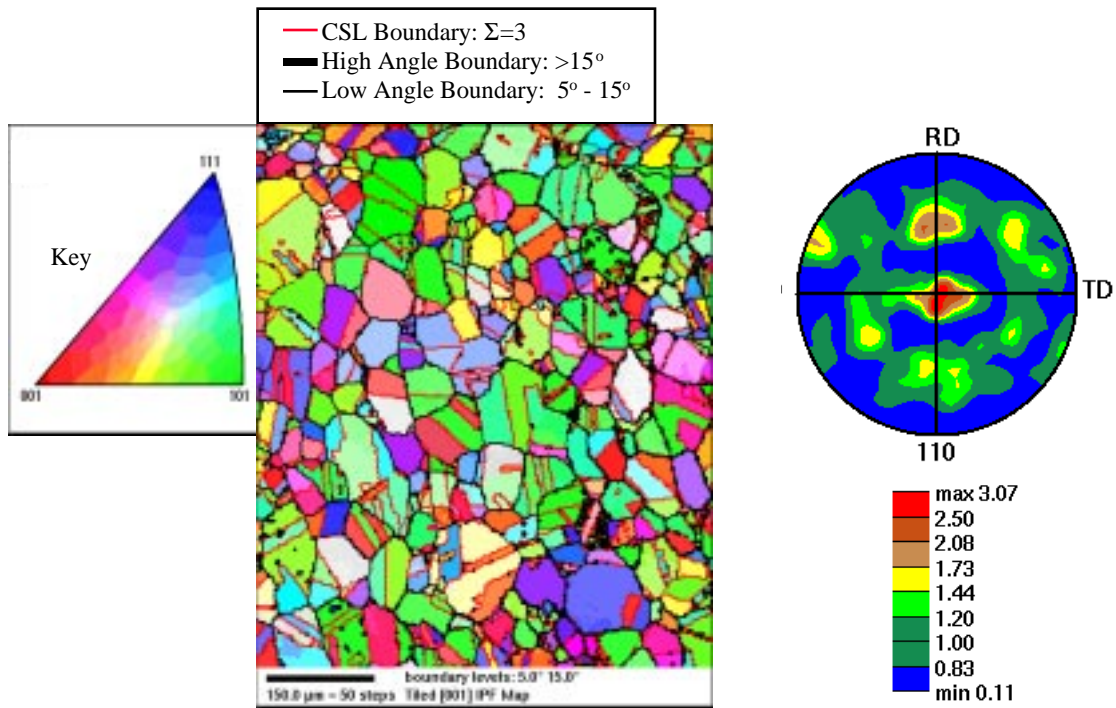
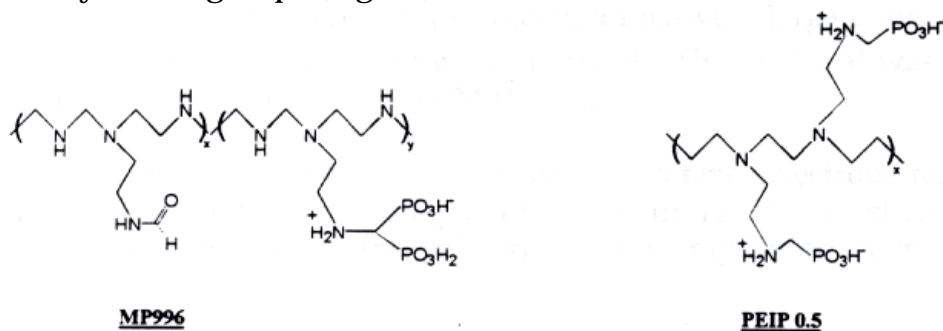


Fig. 9. OIM results from recrystallized 304 SS. (A) OIM pattern. (B) (110) pole figure.

Principal Investigator: Gordon Jarvinen and Barbara F. Smith

Status/Accomplishments. Our efforts this quarter have centered on sample preparation and initial laser analysis of our best actinide-binding water-soluble polymers. These polymers have polyethylenimine (PEI) backbones and have phosphonic-acid containing functional groups attached to the tertiary amine groups (Fig. 10)



Experiments regarding the MP996 bisphosphonic acid and the PEIP half-functionalized phosphonic acid water-soluble polymers involved

- (1) preparing the europium complex of each at various pH points and metal-to-ligand ratios,
- (2) stabilizing the pH for solid sample preparation,
- (3) isolation of permeate, retentate, and precipitation materials for fluorescence analysis, and

(4) acquisition of steady-state and fluorescence lifetime data for structural correlation studies.

In additional studies this quarter, we prepared and characterized other model complexes relevant to this work. The europium complexes of dimethylaminoethylene diphosphonic acid, aminoethylenediphosphonic acid, polyethylenimine, and europium hydroxide were each prepared, isolated, and spectroscopically interrogated.

We began and are continuing data reduction and interpretation both from the europium-doped phosphonic acid polymers and the model compounds that were examined this quarter.

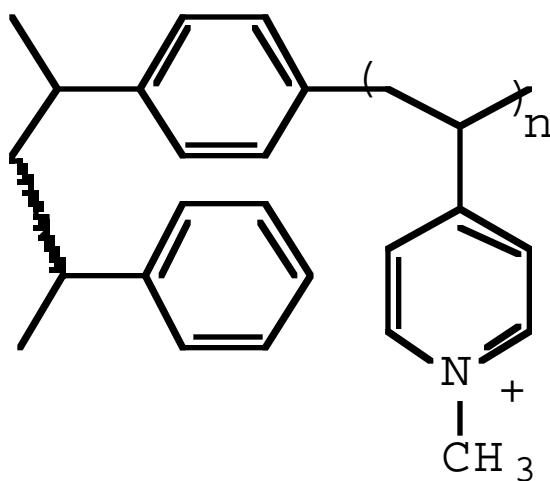
Core Technology:
Separations—Polymer Foams

Principal Investigator: Gordon Jarvinen and Betty Jorgensen

Task Description. This task investigates metal uptake on foams containing graft-polymerized ligands for potential 94-1 application.

Status/Accomplishments.

Plutonium Uptake on Methylpyridinium Foams. Superior performance is shown by Reillex™ HPQ resin beads for uptake and separation of plutonium compared to other resin beads. Reillex™ HPQ is a vinylpyridine resin quaternized with a methyl group. In earlier experiments, we prepared vinylpyridine functionalized foams and tested them for plutonium uptake. We saw fairly good uptake. The vinylpyridine functionalized foams were reacted with methylbromide to give the methylpyridinium functionality found in the Reillex™ HPQ resins. The structure of this foam is shown in Fig. 11.



$n = 1-8$

Fig. 11. Structure of vinylpyridine functionalized foam reacted with methylbromide to give the methylpyridinium functionality found in Reillex™ HPQ resins.

The foams were tested for uptake of plutonium. The plutonium test solution consisted of 6 ml of nitric acid containing 18 mg plutonium and 0.125 grams of foam. Several samples were tested. The best results obtained are as shown in Table 2.

Table 2. Results for Foams Tested for Uptake of Plutonium

	Current Results		Previous Results
Nitric Acid	7 M	1 M	7 M
30 min K_d	59	8.2	48
2 h K_d	Not Tested	Not Tested	160
6 h K_d	208	9.0	842
24 h K_d	481	9.1	Not Tested

As can be seen, quaternization of the methylpyridinium foams did not result in better uptake. This result was quite unexpected, and the reason for the lower plutonium uptake is not clear at this time. Plutonium is known to extract better into organic phases than aqueous phases. Possibly including a copolymer that mimics an organic phase with the vinylpyridine would aid in the extraction of plutonium. The copolymer would also provide spacer groups between the pyridine functionalities that could optimize the distance for binding plutonium most effectively.

Foam Columns. We have sealed foams into glass columns such as those used for ion exchange and chromatography. Sealing of the foam to the column walls is essential to force the waste solution through the foams and to prevent channeling along the sides. A highly acid-resistant adhesive was used so the foams can be used for plutonium solutions in nitric acid. Foams sealed into columns have a significant advantage over resin bead columns. The foams do not swell when hydrated, unlike many resin beads. Swelling causes a change in volume and may create sufficient pressure in closed systems to break glass. Two columns have been made. One column has an 11-in.-long, 1.5-in.-diam foam monolith inside a glass column with a slightly larger diameter. The other column is 6 in. long with a 0.75-in. diameter. The foams will be filled with a plutonium extractant such as CMPO derivatives and tested for plutonium uptake. The current method of sealing the foams is somewhat time-consuming, since the adhesive soaks into the foam interior. This necessitates using several thin coatings to seal the foam. Alternative methods are under investigation.

University Collaboration. Researchers at the University of Tennessee have prepared foams with immobilized beta-ketophosphonate, diphosphonate, monophosphonate, and triethylene glycol ligands. The foams have crosslink levels of 8% and 15% divinylbenzene. They have established conditions that yield uniformly functionalized foams which retain their original form. Inner and outer regions of the foam have identical characterization data.

Having shown that foams can be functionalized as routinely as polymer beads, university researchers shifted the focus to column studies with the primary challenge being to achieve a tight bond between the glass column and the foam. They have found that using a glass column slightly larger in diameter than the foam allows placing the foam within the column and filling the empty space with very fine alumina powder. The foam provides less resistance to passage of the liquid than the alumina. Under these conditions, a 15% DVB foam functionalized with phosphonic acid ligands contacted with 10^{-4} N copper nitrate in 0.01 N nitric acid with a 9-min elution time complexes the Cu^{2+} to give a distribution coefficient of 1344. Under identical conditions, a comparable amount of similarly crosslinked beads gives a distribution coefficient of 273. Control experiments show that passage of the solution through the alumina packing is negligible; additionally, alumina itself will not complex copper ions.

It has therefore been shown during the current contract period that polymer foams can be uniformly functionalized with a wide array of ligands while maintaining their structural integrity and that their performance in column elutions of metal-containing solutions can exceed the performance displayed by comparably crosslinked beads.

Core Technology:
Material Science—Thermodynamics

Principal Investigator: Mark A. Williamson

Task Description. In this task, we study the vaporization chemistry, thermodynamics, and phase behavior of plutonium- and americium-bearing compounds relevant to 94-1 stabilization technologies. Currently we are investigating the phase behavior of plutonium and americium oxychloride that could be present in the salt matrices destined for the distillation process. The phase behavior and thermodynamic data collected in this study will improve the understanding and modeling of the distillation process.

The former *Mineral Waste Form* task has been merged with this one. Determining the synthesis parameters for the preparation of zircon (ZrSiO_4) via cold pressing and sintering of the component oxides was the focus of this report period for mineral waste forms. We pursued synthesis via cold pressing and sintering because it was less equipment-intensive and more accessible than hot isostatic pressing (HIP), which was used initially. Thus, samples could be prepared at a much faster rate and the effects of various synthesis parameters examined in a more efficient manner.

Status/Accomplishments.

Thermodynamics. This quarter, our work consisted of repair of the quadrupole mass spectrometer (QMS) system. Problems in the C50TM electronics system were identified and repaired. The system resonance was optimized according to the procedure described in the operators manual provided by the manufacturer, Extrel.

Perfluorotributylamine, a calibration compound that provides mass markers up to mass 614, was leaked into the mass spectrometer to verify the mass scale. Initially the mass scale was nonlinear with a mass defect of about +30 amu at high mass and -5 amu at low mass. We adjusted potentiometers on the mass command board according to the linearization procedure described in the Extrel manual. We ordered replacements for two precision potentiometers that were found to be out of specification. Although the two potentiometers were out of specification, the mass scale now has a zero mass defect at 502 amu, -4 at 131 amu, and -2 at 69 amu. Replacing the defective potentiometers should eliminate the mass defect at low mass. The CMR building was placed in stand-down before the defective potentiometers could be replaced.

Activities in the CMR are being brought back on line according in accordance with a resumption approach. Limited thermochemistry operations should be

on-line in mid-October. Normal thermochemistry operations should resume in early November. When normal operations resume, the two defective potentiometers in the mass command board will be replaced, the mass scale calibration will be completed, the sensitivity of the quadrupole mass spectrometer system will be established, and AmOCl vaporization experiments will be initiated.

Mineral Waste Forms. We conducted comminution studies on powder mixtures of the component oxides of zircon, ZrO_2 ($<3\ \mu\text{m}$) and SiO_2 ($<44\ \mu\text{m}$), to determine the effects of milling time, grinding media, dispersant, sintering temperature, sintering time, and stoichiometry on the reaction yield and the microstructure of zircon. A vibratory mill was used for the comminution studies. Two grinding media—tungsten carbide and zirconia—with different density and hardness were used to determine the efficiency of grinding. The efficiency of grinding was determined directly by the reaction yields after sintering at the same high temperature, 1400°C , for same duration, 8 h. The reaction yields were determined by Rietveld analysis of x-ray powder diffraction patterns taken on sintered samples.

We prepared a total of 34 samples by grinding, cold pressing, and sintering, and analyzed them using x-ray powder diffraction. The results are summarized in Table 3. The effect of milling time and stoichiometry on the reaction yield is indicated in Fig. 12. For each run, a 10 g batch of mixture was prepared and ground for preselected time. An approximately 0.5-g sample was then taken, cold-pressed at approximately 50,000 psi, and sintered at 1400°C for 8 h. These results show that dry grinding is not efficient, mainly due to the conglomeration of powder mixtures. Nevertheless, higher yields, compared to previous yields of $<30\ \text{wt}\%$ obtained from hot isostatic pressing, can be achieved by long duration of grinding. This figure also shows that reaction yield can be increased by 10% if the sintering temperature is increased from 1400°C to 1500°C . The results also suggest that reaction yield is increased with higher concentrations of SiO_2 .

A major breakthrough has been achieved in obtaining 100% yield in the synthesis of zircon within a short period of time without much preparation to the starting material. Unless high density is desired in the final product, this finding allows the synthesis to be accomplished without the harsh conditions of high temperature and high pressure, such as hot isostatic pressing, and thus making the process safer and more economical. However, the preparation techniques developed during these studies will still be applied to synthesis of zircon via HIP, should a high density product ever be desired. For large scale fabrication of plutonium-bearing zircon, the existing MOX fuel process facility appears to be adequate. An SOP for conducting the synthesis of PuSiO_4 in the MOX facility in PF-4 at TA-55 has been proposed and is under management review.

Table 3. Summary of Reaction Yields from Comminution Studies.

Sample	Product composition (wt%)			Remarks
	Zircon	SiO ₂	ZrO ₂	
z40Si	5.5	25.8	68.7	Ball-milled, 18 h
z50Si	10.5	33.0	56.5	Ball-milled, 18 h
z60Si	15.3	39.7	45.0	Ball-milled, 18 h
z40Si-spex	8.2	22.5	69.3	Spex-milled, 30 min
z50Si-spex	27.3	26.2	46.6	Spex-milled, 30 min
z60Si-spex	28.4	36.6	35.0	Spex-milled, 30 min
spex-45	32.5	34.8	32.7	60 mol% silica, 1400°C
spex-60	34.5	34.0	31.5	60 mol% silica, 1400°C
spex-75	38.2	32.4	29.3	60 mol% silica, 1400°C
spex-120	45.2	31.1	23.7	60 mol% silica, 1400°C
spex-240	59.8	24.7	15.5	60 mol% silica, 1400°C
spex-360	68.1	22.3	9.6	60 mol% silica, 1400°C
spex-420	72.4	19.8	7.8	60 mol% silica, 1400°C
spex-420-1500	83.9	15.0	1.1	60 mol% silica, 1500°C
sz-spex-120	26.1	27.0	46.9	50 mol% silica, 1400°C
sz-spex-240	36.2	24.0	39.9	50 mol% silica, 1400°C
sz-spex-360	43.8	20.6	35.6	50 mol% silica, 1400°C
sz-spex-480	49.6	18.5	31.9	50 mol% silica, 1400°C
sz-spex-480-1500	63.7	12.3	24.1	50 mol% silica, 1500°C
wcww-15	29.5	26.5	44.0	Wet, WC, 5 mL water
wcww-30	40.3	22.7	37.0	Wet, WC, 5 mL water
wc10w-60	96.0	2.0	2.0	Wet, WC, 10 mL water
wc-w-30	19.0	30.0	51.0	Wet, WC, 10 mL methanol
wc-w-60	33.5	25.4	41.2	Wet, WC, 10 mL methanol
w-z-5	16.6	32.0	51.4	Wet, zirconia, 5 mL methanol
w-z-15	36.3	22.9	40.8	Wet, zirconia, 5 mL methanol
w-spex-60	85.6	0.0	14.4	Wet, zirconia, 10 mL methanol
w-spex-120	78.5	0.0	21.5	Wet, zirconia, 10 mL methanol
zww-15	22.2	25.0	52.8	Wet, zirconia, 5 mL water
zww-30	43.5	16.0	40.5	Wet, zirconia, 5 mL water
zww-30a	70.0	10.2	19.7	Wet, zirconia, 10 mL water
zww-60	93.7	0.0	6.3	Wet, zirconia, 10 mL water
zww-45	95.7	0.0	4.3	Wet, zirconia, 10 mL water, 51 mol% silica
zw3w-30	85.6	6.7	7.7	Wet, zirconia, 15 mL water, 51 mol% silica

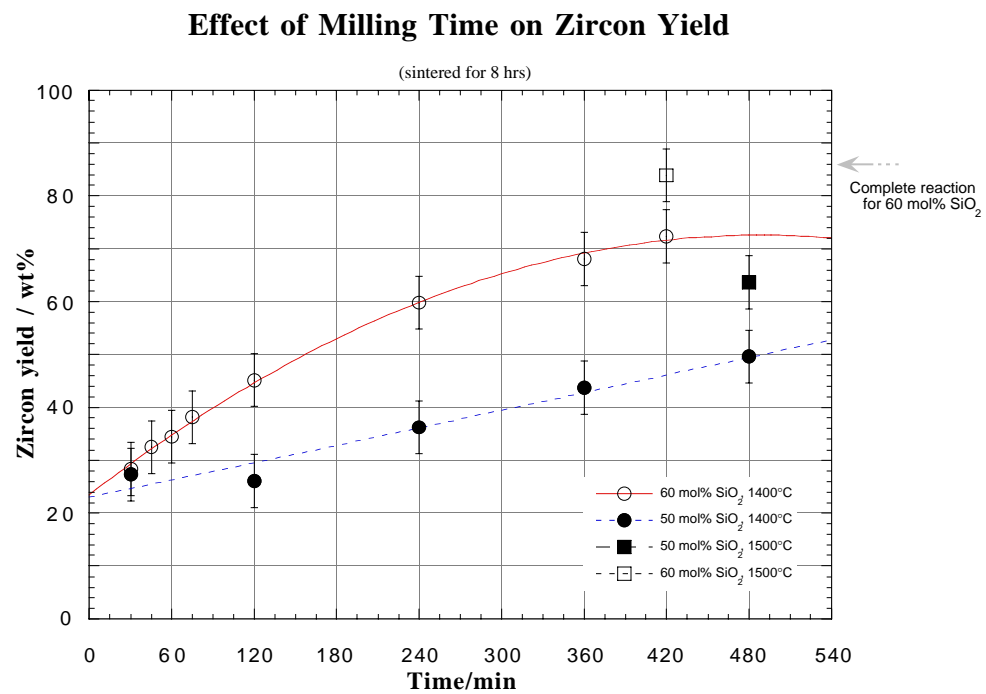


Fig. 1. Effect of stoichiometry and sintering temperature.

Fig. 12. Effect of stoichiometry and sintering temperatures.

Core Technology:

Synthesis and Structural Characterization of Plutonium (IV) and (VI) Phosphates

Principal Investigators: Wolfgang Runde and Kirk Veirs

Task Description. Phosphate coordination plays a significant role in actinide chemistry and potential stabilization processes such as nitric/phosphoric acid treatment of combustibles. Our objective is to develop a fundamental understanding of plutonium phosphate chemistry for synthesis of plutonium phosphate compounds, characterization of the solid state, and chemical behavior under radiolysis and aqueous conditions. The work supports plutonium solubility studies .

Status/Accomplishments. During this quarter, hydrothermal synthesis yielded a novel light green U(IV) solid, P1. Relatively few uranium (IV) phosphate compounds have been reported but include mixed valence state compounds where U(IV) and U(VI) are both present, often in a 1:1 ratio, as in $\text{U}(\text{UO}_2)(\text{PO}_4)_2$. There are few reported examples of U(IV) compounds in the literature prepared by hydrothermal methods. The powder XRD pattern shown below in Fig. 13 indicates that the compound is reasonably pure. The most intense peak occurs in a region where its presence may indicate a layered compound.

The uv-vis spectra of solutions of P1 in concentrated phosphoric acid and U(IV) in 0.2 M perchloric acid are shown in Fig. 14. The U(IV) peaks are closely matched. The slight differences in peak shift may be attributed to the different solvents employed. A sample of U(IV) in H_3PO_4 is currently being examined. The signature U(VI) peaks centered at approximately 420 nm are absent from both spectra.

Attempts are underway to generate single crystals of this compound for structural analysis. Complete characterization by FTIR, Raman, and fluorescence spectroscopic methods is nearing completion. In addition, efforts to prepare additional new U(IV) phosphates and analogous Pu(IV) compounds are ongoing.

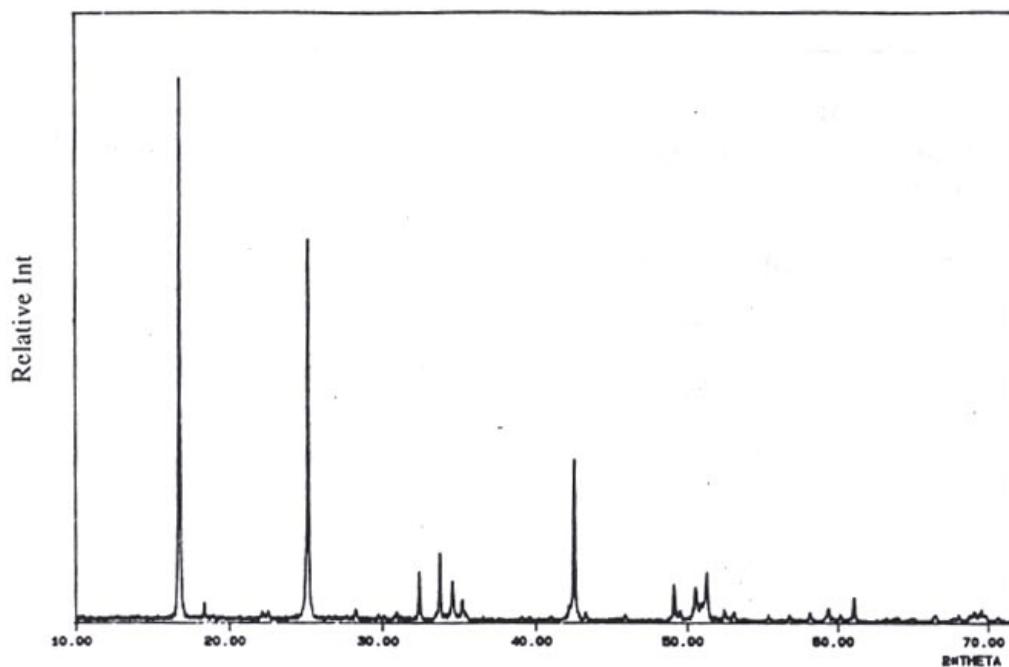


Fig. 13. Powder XRD pattern of P1 shown expanded from 5 to 72°, 2 θ , collected at room temperature.

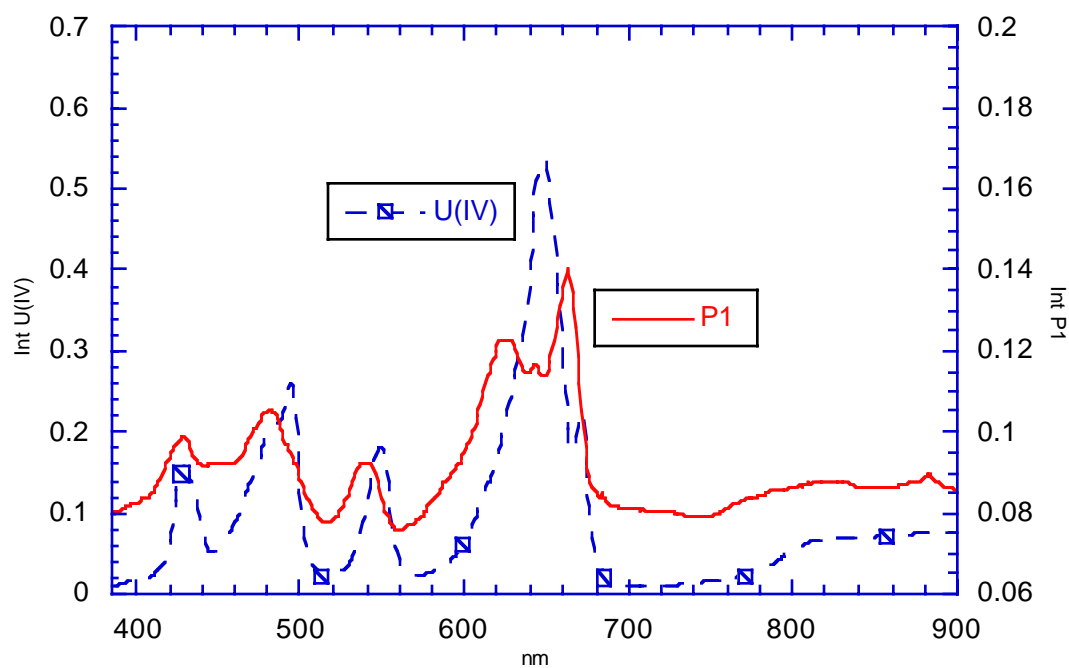


Fig. 14. uv-vis spectra of P1 in 85% H_3PO_4 and U(IV) in 0.2 M HClO_4 .

Core Technology:
Plutonium Phosphate Solution Chemistry

Principle Investigator: David G. Karraker, Savannah River Site

Task Description. An attractive process for destruction of combustible glove-box residues involves oxidation of organic material by nitric acid or hydrogen peroxide in a concentrated phosphoric acid (H_3PO_4)¹. After organic material is oxidized, plutonium and other metal ions will accumulate in the H_3PO_4 solution. This study of the chemistry of plutonium in concentrated phosphoric acid is aimed at determining the properties of plutonium ions in concentrated phosphoric acid and investigating methods for recovering plutonium and recycling H_3PO_4 .

Status/Accomplishments. The extraction of plutonium by trioctylphosphine oxide (TOPO) and diphenyl-N,N'-dibutylcarbamoylmethylene phosphine oxide (CMPO) resins was tested from 1.87, 4, and 6 M H_3PO_4 solutions. The TOPO resin was prepared by mixing a methanol solution of TOPO with Rohm and Haas XAD-7 polystyrene resin, and then removing the methanol by vacuum evaporation. The CMPO resin was prepared in the same fashion. The resins were loaded to 5 g TOPO/5g resin and 3.7 g CMPO/10 g resin. The resins and the solution were mixed for 30 min or more before sampling.

The results presented in the Table 4 are K_d values, where $K_d = (C_0 - C)C \times \text{wt of resin/resin dry wt}$. C_0 is the initial concentration of Pu(IV) in solution, C the concentration at the time of sampling. The results showed that TOPO was more effective in stronger acid, while CMPO was more effective in weaker acid.

Table 4. K_d Extraction Values

H_3PO_4 , M	TOPO K_d	CMPO K_d
1.87	2.57	4.48
7.0	2.41	1.91
6.0	3.90	1.41

The more attractive prospect for plutonium recovery from H_3PO_4 solutions is the TOPO resin, since it recovers from the stronger acid. However, a column test found that the capacity was too low to be useful. Plutonium adsorbed for only two column volumes; the next two column volumes of 6 M H_3PO_4 eluted the adsorbed plutonium.

Core Technology:
Molten Salt/Nonaqueous Electrochemistry

Principle Investigator: Wayne Smith

Task Description. Even though pyrochemical processes have for a number of years been used to recover and purify plutonium and other actinides, little is known about the chemistry that occurs within these molten salt solvent systems. Part of the difficulty in studying chemical reactions in the molten salts is due to the extreme conditions, $>600^{\circ}\text{C}$, and the corrosive nature of the salts, which preclude the use of standard characterization techniques and equipment. One way to circumvent these problems is to study the reactions under more benign conditions. This can be accomplished by the use of room temperature molten salt systems. Room temperature molten salts (RTMS) consist of approximately equal mixtures of aluminum trichloride and an organic chloride salt, usually methyl-ethyl-imidazolium chloride. Like the salts used in the pyrochemical processes they are chloride based, yet their melting points are at or near room temperature. Therefore it is expected that the actinide reaction chemistry observed and measured in RTMS systems will be similar to what takes place in the higher temperature melts, but at a slower rate.

The original project scope was to completely characterize the reaction chemistry of uranium in the RTMS systems. The results of this study would then be used as a benchmark to compare results obtained for the other actinides, including plutonium and americium. However, the project was rescoped in mid-year to address issues more relevant to the Defense Nuclear Facilities Safety Board (DNFSB) 94-1 R&D project.

Status/Accomplishments.

Uranium results. A unique feature of the RTMS systems is the ability to change the acidity/basicity of the melt by varying the aluminum chloride/organic chloride ratio. This is equivalent to adjusting the pH in aqueous solutions, which can have a pronounced effect on the stability or reactivity of dissolved species. In basic RTMS melts, the chemistry and electrochemistry of uranium is quite simple. Uranium(IV) is reversibly reduced to U(III). When starting with uranium(VI) as UO_2^{2+} , there is an irreversible two electron reduction process followed by a reversible one electron reduction process. The reactions can be represented as:



These reactions parallel those observed for uranium in aqueous solution.

In acidic RTMS melts, in the absence of oxygen, uranium(IV) is reversibly reduced to U(III) and reversibly oxidized to U(V) and U(VI). The U(V) species is quite stable and can be produced in quantitative yield by controlled potential electrolysis. This behavior is in marked contrast to that observed in aqueous solution where U(V) is quite unstable, reacting with water to form UO_2^+ , which can then undergo further oxidation to UO_2^{2+} .

When UO_2^{2+} is added to an acidic melt there is a relatively fast reaction with the solvent followed by a slower reaction that ultimately yields U^{5+} . The reaction scheme is provided in Fig. 15.

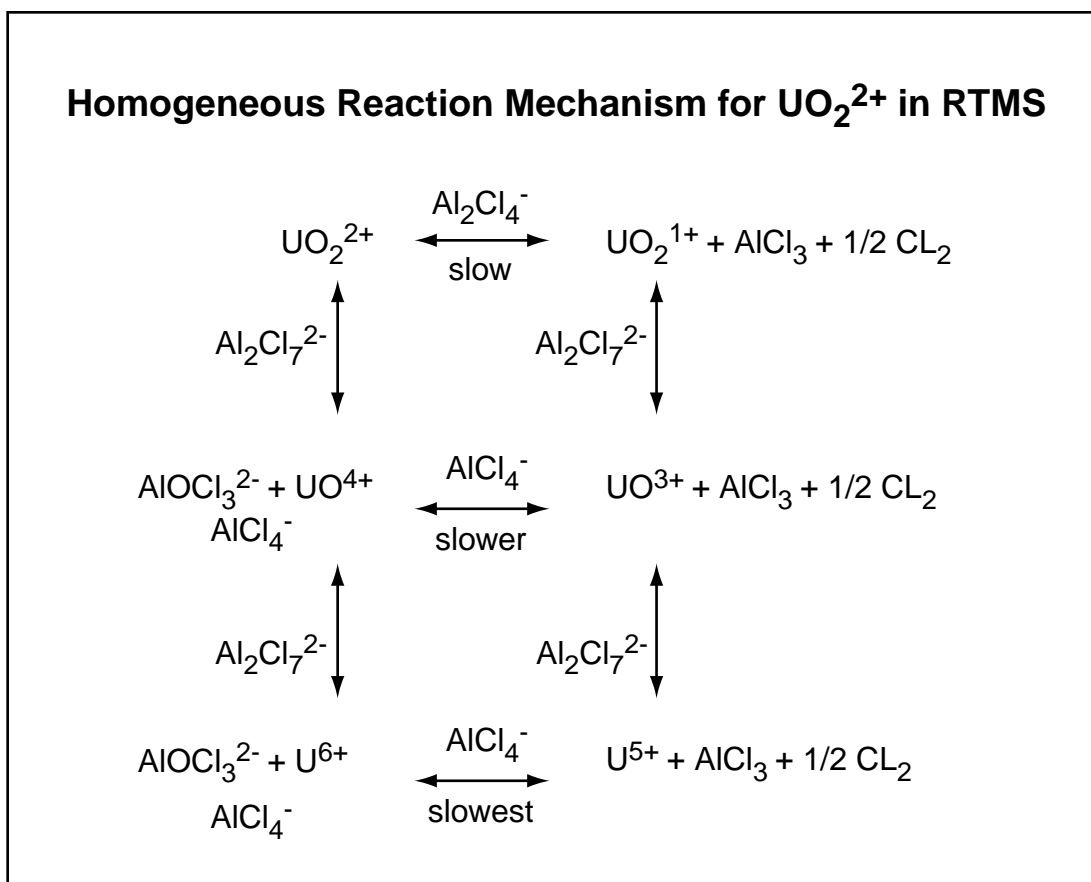


Fig. 15. Homogeneous reaction mechanism for UO_2^{2+} in an acidic RTMS melt.

The first step in the mechanism is an acid/base reaction between the basic UO_2^{2+} and the acidic solvent. The solvent removes oxygen atoms from the uranyl ion to form UO^{4+} and U^{6+} respectively. Both species can then participate in electron exchange reactions with the solvents to form uranium(V) species. Although the reaction with U^{6+} should be much faster than the reaction with UO^{4+} , there is a

much greater concentration of UO^{4+} in solution owing to the nature of the acid/base equilibrium, so the reaction most likely proceeds by both lower horizontal pathways.

The behavior of uranium in the high temperature molten salts should be similar to that observed in basic RTMS, as given by reactions (1) and (2) above. One additional reaction that can occur in the high temperature melts is the reduction of U^{3+} to U^0 . This reaction is due to the more negative reduction potential that can be applied in the high temperature melts.

APPENDIX

FY 1997 94-1 R&D Publications, Reports, Presentations, Patents, License

Journal Publications

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